OCCUPATIONAL EXPOSURES TO MISTS AND VAPOURS FROM SULFURIC ACID AND OTHER STRONG INORGANIC ACIDS

1. Exposure Data

1.1 Introduction

Acidity has been defined in various ways. The Arrhenius concept (sometimes referred to as the aqueous concept) of acids and bases defines an acid as any substance that can increase the concentration of hydronium ion, H_3O^+, in aqueous solution. A somewhat more general approach, proposed independently in 1923 by the Danish chemist, J.N. Brønsted, and the British chemist, T.M. Lowry, defines an acid as a substance that can donate a proton (i.e., a hydrogen ion, H^+) to some other substance (Brady & Humiston, 1978).

The position of equilibrium in an acid–base reaction indicates the relative strengths of the acids and bases involved. Hydrogen chloride is a strong acid in water because the position of equilibrium in the ionization reaction lies far to the right [$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$]. Hydrogen fluoride, however, is said to be a weak acid because it is only very slightly dissociated in water (about 3% of a 1 M solution at room temperature). The strength of an acid is usually represented by the pK_a value, which is the negative logarithm (to the base 10) of the acid ionization (dissociation) constant, K_a, for the reaction in question. The stronger the acid, the lower the pK_a value; the weaker the acid, the higher the pK_a value. Some acids, like sulfuric (H_2SO_4) and phosphoric (H_3PO_4), can donate more than one proton; such acids have separate ionization constants for the loss of each proton.

Table 1 presents the dissociation constants and boiling-points for several acids; although the subject of this monograph is occupational exposure to strong inorganic acids, some organic acids are included in the table for comparison. The principal acids of interest for this monograph are sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid. Exposure to chromic acid was evaluated previously (IARC, 1990).

Strong inorganic acids may be present in air in three different forms: mist, vapour and gas. The term ‘mist’ refers to a liquid aerosol formed by condensation of a vapour or atomization of a liquid (Hinds, 1985). A vapour is defined as the gaseous state of a substance which is a liquid or solid at normal temperature and pressure (Fowler & Fowler, 1964). Hydrochloric acid is a gas, which can also be present in workplace air as a mist when dissolved in water. Nitric, sulfuric and phosphoric acids are liquids that may be present in air as mists or vapours; they are, however, present primarily as mists because of their low volatility and their affinity for water. Sulfuric and nitric acids may further release sulfur trioxide vapours and gaseous nitrogen oxides, respectively, especially at high concentrations and elevated temperatures in the absence of atmospheric moisture (Sax & Lewis, 1987). The sampling

Table 1. Dissociation constants (pK_a) and boiling-points of some acids

Acid	pK_a[a]	Boiling-point (°C)
Hydrobromic acid	< 0	-67.0[b]
Hydrochloric acid	< 0	-84.9[b]
Chlorosulfonic acid	< 0	158[c]
Sulfuric acid	< 0 (step 1)[d] 1.92 (step 2)	315-338[c]
Methanesulfonic acid	< 0	200[c]
Ethanesulfonic acid	< 0	123 at 1 mm Hg [133.3 Pa]
Nitric acid	< 0	83[e]
Chromic acid (chromium trioxide)	0.74 (step 1) 6.49 (step 2)	Decomposes at 250 °C[e]
Perchloric acid	1.77	19 at 11 mm Hg [1467 Pa][e]
Phosphoric acid	2.12 (step 1) 7.21 (step 2) 12.67 (step 3)	261[f]
Chloroacetic acid	2.85	187.8[d]
Hydrofluoric acid	3.45	19.54[d]
Formic acid	3.75	100.7[d]

[a] From Guthrie (1978); Weast (1989). For acids with pK_a less than 0, there is no generally satisfactory way to measure the pK_a in aqueous solutions; reported pK_as were measured at 18–25 °C.

[b] From Weast (1989)

[c] From Sax & Lewis (1987)

[d] Step 1, release of first hydrogen; step 2, release of second hydrogen

[e] From Budavari (1989)

[f] From Hudson & Dolan (1982); Eller (1984)

techniques used traditionally do not allow differentiation between the liquid and gaseous forms of the acids nor determination of the distribution of particle sizes for the mists. Few data are available on particle size distribution of acid mists in the work environment.

The following section addresses several industries in which strong inorganic acids are manufactured or used in a manufacturing process and for which epidemiological studies were available. These are isopropanol manufacture, synthetic ethanol manufacture, pickling and other acid treatment of metals, sulfuric acid manufacture, soap and detergent manufacture, nitric acid manufacture, phosphate fertilizer manufacture and lead battery (accumulator) manufacture.

1.2 Description of the industries

1.2.1 *Isopropanol manufacture* (see also IARC, 1977, 1987)

Isopropanol is claimed by some to be the first petrochemical. During the latter part of the First World War, isopropanol was manufactured by the Ellis process which was quite similar to that used today. The basic chemistry of the process is the reaction of propylene with sulfuric acid to form isopropyl sulfates, which are then hydrolysed to isopropanol (Haberstroh & Collins, 1983a).

In the 'strong-acid process' (indirect hydration), propylene gas (C_3-feedstock, 40–60% propylene) and 88–93% sulfuric acid are fed to a reactor maintained at 25–30°C. The diisopropyl sulfate so formed is hydrolysed with hot water to give crude isopropanol, isopropyl ether and approximately 40% sulfuric acid. The aqueous alcohol is separated from the light, top-floating layer of isopropyl ether and isopropyl oil (largely polypropylenes composed of 3 and 4 propylene molecules, with less than 1% each of benzene (see IARC, 1987), toluene, alkyl benzenes, polyaromatics, hexane, heptane, acetone, ethanol, isopropanol and isopropyl ether) and is then refined by distillation. In the 'weak-acid process', propylene gas is fed continuously to a series of absorbers containing 60% sulfuric acid maintained at 60–65°C. This reaction produces diisopropyl sulfate, which is distilled and then hydrolysed to form crude isopropanol. This crude alcohol contains isopropyl ether, acetone, traces of methanol, water and oil (the composition of the oil produced in this process has not been reported). Refined isopropanol is obtained by distilling the crude alcohol in a series of columns and removing the impurities. Anhydrous isopropanol is made by breaking the alcohol–water azeotrope by introducing benzene. In the USA, the weak-acid process has replaced the older strong-acid process (Lynch *et al.*, 1979; Papa, 1982; Teta *et al.*, 1992). The reaction of propylene with sulfuric acid is a complex series of reactions in which water plays a major role in determining the concentration of the intermediate alkyl sulfates (Lynch *et al.*, 1979). (See the monograph on diisopropyl sulfate, p. 229.)

Plants built in Europe use a direct hydration process in which propylene and water are reacted in the presence of a catalyst such as phosphoric acid on bentonite. One limitation of this route is that it requires a highly concentrated propylene feed rather than a dilute refinery stream (Papa, 1982).

Production of isopropanol in several countries is presented in Table 2.

Table 2. Trends in production of isopropanol in some countries (thousand tonnes)

Country	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
Brazil	NR	NR	NR	6.7	6.8	6.3	6.0	4.5	5.4	NR	NR
Canada	72.2	73.3	67.2	63.3	62.9	NR	NR	NR	NR	NR	NR
China	NR	NR	NR	12.5	16.7	17.5	17.4	20.4	22.1	NR	NR
India	2.5	NR	2.6	2.9	2.8	NR	NR	NR	NR	NR	NR
Japan	NR	97.9	96.3	90.4	91.5	88.5	84.8	100.6	95.2	102.5	NR
Mexico	12.6	15.6	10.9	11.9	14.1	14.5	11.1	NR	NR	NR	NR
Spain	24.8	23.7	23.4	27.0	26.9	27.3	24.1	19.3	23.8	29.5	NR
USA	832.8	757.0	626.0	548.4	632.3	560.2	590.1	621.9	630.0	668.6	626.0

From Japan Chemical Week (1990); Anon. (1991); Dialog Information Services, (1991); NR, not reported

1.2.2 *Synthetic ethanol manufacture*

Ethanol has been made by fermentation processes throughout human history, and these processes still account for most of the ethanol produced worldwide. With the development of the petrochemical industry in the early twentieth century, however, processes were introduced for the production of synthetic ethanol from ethylene. The original esterification–hydrolysis process for synthetic ethanol has gradually been replaced by direct catalytic hydration of ethylene (Haberstroh & Collins, 1974, 1983b; Kosaric *et al.*, 1987).

The esterification–hydrolysis process (indirect hydration process), first used commercially in 1930, is the older of the two ethylene-based routes and accounted for about 80% of production in the 1960s. This process takes place in two steps: ethylene is absorbed into 94–98% sulfuric acid at about 75 °C, producing a mixture of ethyl hydrogen sulfate and diethyl sulfate (see monograph, p. 213); this mixture is then diluted with water to produce ethanol. The overall yield is about 90% ethanol and 5–10% diethyl ether. The process can be modified to produce diethyl ether by increasing the residence time in the hydrolyser and then recycling the alcohol (Haberstroh & Collins, 1974; Kosaric *et al.*, 1987). The reaction of ethylene with sulfuric acid is a complex series of reactions in which water plays a major role in determining the concentration of the intermediate alkyl sulfates (Lynch *et al.*, 1979). (See the monograph on diethyl sulfate, p. 213.)

The direct hydration process, introduced in 1948, involves a water–ethylene reaction over a phosphoric acid (H_3PO_4) catalyst at about 250–300 °C and 6–8 MPa. The overall yield of ethanol is reported to be greater than 97%. This process has the advantages of higher yields, production of less diethyl ether as a by-product, lower plant maintenance costs, and elimination of the waste and pollution problems that characterized the esterification–hydrolysis route. Of the synthetic ethanol produced in 1970, 48% was made by direct hydration (Haberstroh & Collins, 1974, 1983b).

Several other methods for producing synthetic ethanol have been investigated, including homologation of methanol, carbonylation of methanol and methyl acetate, and catalytic conversion of synthesis gas (Kosaric *et al.*, 1987).

Synthetic ethanol is purified in a simple three-column distillation unit. Recovery is 98%, and the high-grade product contains less than 20 mg/kg of total impurities. To produce anhydrous ethanol, the water–ethanol azeotrope obtained by distillation of the crude synthetic feedstock must be dehydrated. For economic reasons, large distilleries rely mostly on azeotropic distillation for ethanol dehydration. Benzene has been used as an azeotropic dehydrating (entraining) agent in many plants; cyclohexane and ethylene glycol have also been used. Some smaller plants use molecular sieve adsorption techniques to dry the ethanol azeotrope (Kosaric *et al.*, 1987).

Worldwide production of synthetic ethanol in the early 1980s was estimated to be 2.3×10^9 litres/year, with western Europe accounting for 26.7%, North America for 38.6%, Asia (including the USSR) for 31.7%, and other countries (Japan, Israel, South Africa) for 3%. Most of the plants that produce synthetic ethanol are located in industrialized countries; the developing countries produce mainly fermentation ethanol. In the early 1980s in Canada, Germany, Italy and the United Kingdom, approximately 50% of the ethanol produced was by ethylene hydration; the corresponding figure for the USA was around 35% (Kosaric *et al.*, 1987).

1.2.3 *Pickling and other acid treatment of metals*

Pickling is one of the most widely used industrial processes. It is used in small electroplating plants, in automobile manufacturing plants, in steel producing plants and in any plant where coatings are applied to a base metal. Pickling is a descaling process, in which oxides and scale are removed chemically from a metallic surface by immersion in a dilute inorganic acid (up to 25% acid), which is generally, but not exclusively, sulfuric or hydrochloric acid (see monograph, p. 189). While other descaling processes are in use, pickling is the most widely applied (Morse, 1983).

(*a*) *Processes and acids*

Although various kinds of pickling process are encountered under many different names, they can be classified into three general types: (i) stationary or vat pickling, (ii) batch pickling and (iii) continuous pickling. The degree of acid splashing, gas evolution and mist formation vary with the method employed. Stationary or vat pickling is used mostly within the electroplating industry, whereas batch and continuous pickling are generally used in large production industries. In vat pickling, the product is immersed in an acid solution and generally remains stationary, while the solution is kept in motion. In batch pickling, several pieces of the same product are immersed in the acid solution and are generally kept in motion. In continuous pickling, the product is usually a steel strip, which is uncoiled and passed in a horizontal or vertical direction through acid and water-rinse tanks or sprays (Morse, 1983).

Traditional acid pickling solutions are based on inhibited sulfuric, hydrochloric or phosphoric acids; nitric, hydrofluoric and chromic acids are used less frequently. The acids may be used separately, in combination or sequentially at various concentrations and temperatures, depending on the metal being treated, the degree and type of scale and the intended use of the treated metal surface. Schneberger (1981) reviewed typical processes for several categories of metal, including stainless-steel and high-nickel alloys, ferrous metals other than stainless-steel, cuprous metals (copper, brasses and bronzes), aluminium and its alloys, magnesium and zinc and galvanized steel.

Pickling underwent little technological change until fairly recently. In the steel industry, however, where sulfuric acid pickling was formerly used almost exclusively, there is now a trend toward hydrochloric acid pickling in continuous pickling lines. Choice of a particular type of pickling operation is chiefly dependent upon the product to be cleaned. For example, acid cleaning in batch electroplating plants and the pickling of steel bars and plates are generally done by the vat method. Some steel sheet and coils of steel rods and wire are cleaned by the batch method, whereas almost all steel strip is cleaned in high-speed (up to 300 m/min), continuous pickling lines (Morse, 1983).

In some stationary pickling lines, a separate alkaline vat is used to neutralize the acid; in most pickling lines in large production industries, however, water-rinse tanks remove the acid. The rate of pickling, and consequently of metal loss, is dependent on a number of factors, including: acid concentration, temperature of solution, time in bath, percentage of iron compounds in bath, inhibitors present and agitation of the solution. In any pickling process, descaling within a given time can be accomplished by using a high acid concentration at a low temperature or a low acid concentration at a high temperature (Morse, 1983). The major cause of escape of acid mist or vapour from acid tanks in pickling is the formation of hydrogen bubbles and steam which carry acid mist from the surface of the solution; the rate of gas formation depends on the factors above, which in turn affect the rate of pickling (Beaumont *et al.*, 1987).

(*b*) *Pickling of stainless-steel*

Pickling is used on a large scale in the manufacture of stainless-steel. The general sequence of operations involved in processing stainless-steel is: hot working, annealing, conditioning (mechanical or chemical), pickling, cold working, annealing, conditioning (chemical or electrolytic or salt bath), pickling, finishing. Some of the steps are repeated as often as necessary to bring the material to the desired thickness. Having been worked by hot or cold rolling, the steel is softened by annealing, during which process oxide forms. The steel is then conditioned for the pickling process, which is necessary to remove the oxide from the stainless-steel surface. In addition to removing this annealing scale, pickling also removes a very thin (1–5 μm) region depleted in chromium between the oxide and the bulk stainless-steel (Covino *et al.*, 1984).

Hot working is the process of mechanical deformation of a material at temperatures above its recrystallization temperature. Annealing is the process of maintaining metal at a specified temperature for a specific length of time and then gradually cooling it at a predetermined rate. This treatment removes the internal strains resulting from hot or cold rolling and eliminates distortions and imperfections; a stronger and more uniform metal results (Covino *et al.*, 1984).

Conditioning is a process used to prepare annealed metal for the pickling process. Its purpose is to alter the annealing scale in order to reduce the time, temperature and acid concentration used in the pickling process. Depending upon the nature of the oxide film, mechanical and/or chemical techniques are used. Abrasive blasting is one of the fastest conditioning techniques; chemical techniques include chemical conditioning, electrolytic acid conditioning, electrolytic neutral conditioning, and salt bath conditioning. Common chemical conditioning processes may involve the use of reducing (sulfuric and hydrochloric) or oxidizing (nitric) acids. There are three basic types of electrolytic conditioning: anodic, cathodic and alternating current; the most common acids associated with electrolytic conditioning are sulfuric and nitric acids. Electrolytic neutral conditioning is similar in mechanical design to electrolytic acid conditioning in that alternating cathodic and anodic electrodes are used to polarize the workpiece and induce oxidation and reduction of the surface scale; but this process involves a sodium sulfate solution instead of an acid. Salt bath treatments can be either reducing, oxidizing or electrolytic (Covino *et al.*, 1984).

The pickling of stainless-steels involves three distinct processes. The first is removal of thermally grown oxide scale to improve the appearance of the metal and to facilitate further cold working of the steel. The second process maximizes the resistance of the final steel product to corrosion by completely dissolving the chromium-depleted zone that is generally formed during short high-temperature anneals in oxidizing environments. The third process dissolves the minimum amount of bulk steel necessary to give the desired whitening effect (Covino *et al.*, 1984).

Stainless-steel and high-nickel alloy scales adhere tightly and are difficult to remove with the acids used for plain steel, although hot 10% sulfuric acid containing 1–2% sodium thiosulfate or hydrosulfite, or 2% hydrofluoric acid with 6–8% ferric chloride, is often effective. Moderate or light scale is removed with 20% nitric acid containing 2–4% hydrofluoric acid. Nitric acid is a widely used pickling agent and does not affect the stainless character of the steel; in fact, these steels are passivated in nitric acid at greater than 20% concentration. Hydrochloric acid may be used as an activator or as a first treatment to remove scale (Schneberger, 1981).

(*c*) *Other processes*

Other processes involving acid treatment of metals, for which some occupational exposure data were available, include electroplating and electrowinning. Electroplating is the application of a metal coating through the action of an electric current. Types of plating include chromium (see IARC, 1990a), nickel (see IARC, 1990a), copper, brass, silver, gold, cadmium (see IARC, 1987), zinc, lead (see IARC, 1987) and tin. Some strong inorganic acids used are chromic, sulfuric, hydrochloric and nitric acids; different solutions are used depending on the metal to be electrodeposited (Soule, 1982). Galvanizing refers specifically to the plating of zinc onto a ferrous metal. Electrowinning, or electrolytic refining, is the process of extracting a metal from its soluble salt using an electrolytic cell (Sax & Lewis, 1987).

1.2.4 *Sulfuric acid manufacture*

In ancient times, sulfuric acid was probably made by distilling nitre (potassium nitrate) and green vitriol (ferrous sulfate heptahydrate). Weathered iron pyrites were usually the source of the green vitriol. Around 1740, the acid was made in England by burning sulfur in the presence of potassium nitrate in a gas balloon flask. The vapours united with water to form acid, which condensed on the walls of the flask. In 1746, the glass balloon flask was replaced by a large lead-lined box or chamber, giving rise to the name ‘chamber process’. In 1827, Gay-Lussac, and in 1859, Glover, changed the circulation of gases in the plant by adding towers, which are now known as Gay-Lussac and Glover towers. These permit the recovery from the exit gases of the nitrogen oxides that are essential to the economic production of ‘chamber acid’. The acid produced by this method has a maximum acid strength of 75–85% H_2SO_4 (West & Duecker, 1974; West & Smith, 1983). Once of great importance in western Europe and North America, chamber process plants have become almost extinct. Whereas the chamber process accounted for about 80% of sulfuric acid production in these regions in 1910, the figure had decreased to about 15% in 1960; and, by 1980, virtually no sulfuric acid was being produced by this process. Today, most sulfuric acid is produced by the contact process, based on technology developed around 1900 and thereafter (West & Duecker, 1974; West & Smith, 1983; Sander *et al.*, 1984).

In the chamber process, chemical reactions involve sulfur dioxide, oxygen, nitrogen oxides and water vapour. A series of intermediate compounds are formed which decompose to yield sulfuric acid and nitrogen oxides. The overall effect is that the sulfur dioxide is oxidized to sulfur trioxide, which combines with water vapour to form sulfuric acid ($2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$). Nitrogen dioxide acts as the oxidant and is reduced to nitric oxide, which must be reoxidized continually by oxygen in the air. When all the sulfur dioxide has been consumed, the nitrogen oxides are absorbed in sulfuric acid in the Gay-Lussac tower as nitrosylsulfuric acid. The solution of nitrosylsulfuric acid (nitrose) from the Gay-Lussac tower is pumped to the denitration (Glover) tower, where heat releases the nitrogen oxides for re-use in the cycle. In the Glover tower, the denitrated sulfuric acid is concentrated to approximately 78%. Part of this acid is returned to the Gay-Lussac tower for recovery of the nitrogen oxides from the exit gases. The balance is available for use or sale (West & Duecker, 1974).

The basic features of the contact process for making sulfuric acid, as practised today, were described in a British patent in 1831. It disclosed that if sulfur dioxide, mixed with oxygen or air, is passed over heated platinum, the sulfur dioxide is rapidly converted to sulfur trioxide, which can be dissolved in water to make sulfuric acid. A demand for acid stronger than that which could be produced readily by the chamber process stimulated this development. The heart of the contact sulfuric acid plant is the converter in which sulfur dioxide is converted catalytically to sulfur trioxide. Over the course of time, a variety of catalysts have been used, including platinum and the oxides of iron, chromium, copper, manganese, titanium, vanadium and other metals. Platinum and iron catalysts were the main catalysts used prior to the First World War. At present, vanadium catalysts in various forms are generally used. The principal steps in a contact plant burning sulfur are: (1) oxidation of sulfur to sulfur dioxide with dry air; (2) cooling of the gas; (3) conversion or oxidation of the sulfur dioxide to sulfur trioxide; (4) cooling of the sulfur trioxide gas; and (5) absorption of the sulfur trioxide in water to produce sulfuric acid (West & Duecker, 1974; West & Smith, 1983; Mannsville Chemical Products, 1987).

Various attempts have been made to increase the conversion of sulfur dioxide to sulfur trioxide. In one of these, the double catalyst–double absorption system, the process flow is modified so that after the second or third pass in the converter the gases are withdrawn and passed through the absorber to remove the sulfur trioxide. The remaining gases are reheated and sent through the last pass over the catalyst; further absorption follows. Increased conversion, up to 99.5–99.7%, is obtained. This process has been used in new sulfuric acid plants in many industrialized countries to meet strict regulatory restrictions on emissions (United Nations Industrial Development Organization, 1978; West & Smith, 1983; Sander *et al.*, 1984).

Sulfur dioxide for sulfuric acid production is obtained from pyrite and pyrrhotite. It can be obtained from calcium sulfate (as natural gypsum or natural anhydrous calcium sulfate) by calcining with coke (Müller-Kühne method) (United Nations Industrial Development Organization, 1978).

Oleum (fuming sulfuric acid), which consists of solutions of sulfur trioxide in 100% sulfuric acid, is produced in contact process plants by adding sulfur trioxide to sulfuric acid in a special oleum tower (Sander *et al.*, 1984).

Users of sulfuric acid confronted with the task of disposing of waste or spent acid find it advantageous to arrange with an independent producer to exchange the waste acid for fresh acid. Methods have been developed which permit such producers to reprocess the waste acid and obtain a product of virgin quality. In addition, they can operate large, centrally located plants which can produce acid at a much lower cost than can small plants. The end-use of sulfuric acid, more than any other factor, determines the location of sulfuric acid plants; however, sulfuric acid plants in which metallurgical gas is used as the source of sulfur are usually located near smelters producing the gas (West & Smith, 1983).

Enormous amounts of spent sulfuric acid are reprocessed, since most of the sulfuric acid used for industrial processes, other than in the fertilizer industry, acts only as a reaction medium and does not form part of the final product. The largest quantities of spent sulfuric acid come from the organic chemical and petrochemical industries. The range of grades of spent sulfuric acid produced in these industries is very wide, from extremely dilute to comparatively concentrated forms, which may at the same time be lightly or heavily contaminated with organic and inorganic compounds. Another important source of spent sulfuric acid is inorganic chemical factories, particularly those for processing titanium dioxide pigment (see IARC, 1989). The spent acid produced is relatively uniform, with about 20–23% sulfuric acid and 7–15% metal sulfates. Spent acids of similar composition are produced in the metallurgical industry from pickling processes. Wash acids from gas cleaning plants (especially in sulfide ore roasting plants) may have widely varying contents of impurities (Sander *et al.*, 1984).

Sulfuric acid is made in numerous grades and strengths. A discussion of the different grades and purities of sulfuric acid is given in the Annex to this monograph.

Production levels of sulfuric acid in a number of countries and regions are presented in Table 3. A more detailed analysis of the worldwide production and movement of sulfuric acid stocks in 1982 is presented in Table 4.

China is the third largest producer of sulfuric acid, after the USA and the USSR. Since 1876, the Chinese sulfuric acid industry has been based on pyrite as the main raw material. With the national emphasis on agricultural production and the consequent demand for phosphate fertilizers, a large number of small-scale sulfuric acid plants utilizing local resources have been constructed throughout China since the 1960s. In 1984, there were more than 400 sulfuric acid plants in China, with the largest plants producing over 550 000 tonnes per year and the smaller plants producing 9 000–36 000 tonnes. About 60% of the sulfuric acid produced in China in the early 1980s was used in the production of phosphate fertilizers (Zengtai, 1984).

1.2.5 *Soap and detergent manufacture*

Soaps are metallic salts of fatty acids. Detergents are substances that reduce the surface tension of water and include soaps and synthetic detergents, such as the linear alkyl sulfonates and alkyl benzene sulfonates (Sax & Lewis, 1987).

Soap is believed to be one of the oldest materials obtained by purposely reacting two chemical substances to get a useful product. The word 'soap' is derived from the latin *sapo*, first used by Pliny the Elder around 75 AD. Although Pliny is credited with the first written reference to soap, its use is believed to have begun long before recorded history. Soap *per se* was probably never actually discovered but evolved from various crude mixtures of alkali and fatty materials (Feierstein & Morgenthaler, 1983).

With time, it was learnt that soap is not a mixture of alkali and fat but results from a chemical reaction, later called saponification; thus, soap-making changed from an art to an industry. Indeed, soap remained the principal cleaning product, or surface active agent, well into the twentieth century. The development of synthetic detergents in the 1930s dramatically reduced world dependence on soap. Nonetheless, a significant market remains for

Table 3. Production of sulfuric acid in a number of countries and regions (thousand tonnes)

Country or region	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
Australia	2 175	1 963	2 027	1 782	1 726	1 773	1 788	1 678	1 818	1 904	1 464
Bulgaria	852	920	916	861	908	810	807	689	840	846	NA
Canada	4 295	4 117	3 131	3 686	4 043	3 890	3 536	3 437	3 805	3 560	3 311
China	7 640	7 810	8 175	8 696	8 172	6 764	7 510	9 620	10 981	11 408	11 689
Czechoslovakia	1 284	1 315	1 252	1 244	1 240	1 297	1 292	1 264	1 249	1 142	1 033
France	4 941	4 498	4 018	4 093	4 490	4 279	4 005	3 909	4 012	4 146	3 768
Germany[a]	5 065	5 038	4 700	4 559	4 515	4 317	4 214	4 159	4 059	3 250	3 352
Hungary	608	573	571	606	549	541	540	573	512	482	244
India	2 320	2 780	2 270	2 270	NA	NA	NA	NA	NA	NA	NA
Italy	2 821	2 539	4 000	4 115	4 250	4 349	4 159	4 350	4 299	3 213	3 303
Japan	6 777	6 572	6 530	6 662	6 458	6 580	6 561	6 541	6 766	6 885	6 887
Korea (Republic of)	1 702	1 304	1 596	1 610	1 975	2 028	1 898	2 039	NA	NA	NA
Poland	3 019	2 776	2 682	2 786	2 770	2 863	2 966	3 149	3 154	3 114	1 850
Romania	1 756	1 814	1 600	1 941	1 915	1 835	1 971	1 693	1 825	1 687	1 112
Taiwan	769	819	685	678	762	733	727	742	664	768	658
United Kingdom	3 375	2 885	2 582	2 582	2 644	2 550	2 325	2 176	2 253	2 152	1 997
USA	40 059	36 961	30 148	33 188	37 922	36 188	32 653	35 612	38 630	39 283	40 171
USSR	23 033	24 095	23 801	24 714	25 338	26 037	27 847	28 531	29 372	28 276	27 300

From Anon. (1984a,b, 1986, 1988, 1991); NA, not available

[a] Figures for 1989 and 1990 are for western Germany only.

Table 4. Worldwide sulfuric acid production and trade in 1982 (thousand tonnes 100% H_2SO_4)

Geographical area	Production	Imports	Exports
World total	130 263	3 185	3 247
Western Europe	24 094	1 143	1 595
Belgium	1 798	492	64
France	3 927	134	154
Germany (western)	3 750	34	766
Italy	2 360	2	39
Netherlands	1 692	179	195
Spain	2 690	48	75
United Kingdom	2 587	115	67
Africa	10 141	124	NA
Morocco	3 072	NA	NA
South Africa	3 382	105	NA
Tunisia	2 525	1	NA
North America	32 490	582	496
Canada	3 131	203	260
USA	29 359	379	237
Central America	2 979	477	2
Mexico	2 920	453	2
South America	3 329	175	6
Argentina	260	NA	NA
Brazil	2 229	91	NA
Chile	460	1	NA
Asia	20 872	329	785
China	8 174	103	0
India	2 232	NA	0
Japan	6 531	NA	0
Republic of Korea	1 596	141	785
Taiwan	680	22	0
Oceania	2 491	1	NA
Australia	1 971	1	NA
New Zealand	520	NA	NA
Eastern Europe	9 136	355	166
Czechoslovakia	1 252	164	2
Germany (eastern)	920	NA	6
Poland	2 682	NA	94
Romania	1 669	NA	NA
Yugoslavia	1 120	93	NA
USSR	23 801	90	197

From Sander *et al.* (1984); NA, not available soap-based products, for personal use, primarily as bars, and for industrial use (Feierstein & Morgenthaler, 1983).

Free fatty acids are a raw material not only for soap but increasingly for other chemical products. Although fatty acids are sometimes synthesized, most of those used commercially are produced by the hydrolysis of naturally occurring fats and oils. Fatty acids have been produced by four basic processes: saponification of fats followed by acidulation; the Twitchell process; batch autoclave splitting; and continuous high-pressure, high-temperature hydrolysis. The Twitchell process is described in detail as it is the only process in which a strong acid is used (Feierstein & Morgenthaler, 1983).

The Twitchell process is batch acid hydrolysis of fats at atmospheric pressure in the presence of a catalyst called Twitchell's reagent. The original Twitchell's reagent was benzenestearosulfonic acid, but sulfonated petroleum products were commonly used later. After impurities have been removed, the fats are mixed with water, the catalyst (0.75–1.25%) and a small amount of sulfuric acid (0.5–1.0%) and are boiled with steam for one to two days. Spent water is removed and replaced with fresh water and sulfuric acid, and then another boiling cycle is conducted. After two to four boiling cycles, the hydrolysis reaction approaches completion, and the crude fatty acids are drawn off for purification. While the Twitchell process is the simplest to run, it has several drawbacks compared to more modern techniques, one of which is the emission of noxious, acidic fumes (Feierstein & Morgenthaler, 1983).

Alkylbenzene sulfonates account for approximately 50% of the total volume of synthetic anionic detergents used in liquid and spray-dried formulations. Two chemicals are routinely used for sulfonation: oleum (fuming sulfuric acid) and sulfur trioxide; the latter has gained increased popularity in recent years. The oleum process normally yields sulfonic acid of 88–91% purity; the remainder, after neutralization, consists of sulfuric acid and a small amount of unsulfonated oils. The air–sulfur trioxide process normally produces a 95–98% pure sulfonic acid, the remainder consisting of sodium sulfate after neutralization. Another process for making anionic surfactants is sulfation of fatty alcohols or ethoxylated fatty alcohols and alpha olefins. Sulfamic acid and chlorosulfonic acid have also been used in commercial sulfation (Feierstein & Morgenthaler, 1983).

1.2.6 *Nitric acid manufacture*

Nitric acid has been known since the thirteenth century. Glauber synthesized it from strong sulfuric acid and sodium nitrate; however, it was Lavoisier who showed that nitric acid contained oxygen and Cavendish who showed that it could be made from moist air with an electric spark. In the oldest methods used, Chile saltpetre (sodium nitrate) was reacted with concentrated sulfuric acid in heated cast iron retorts; the evolved nitric acid vapours were condensed and collected in stoneware vessels (Green & Li, 1983).

Nitric acid is currently made by oxidation of ammonia with air over a precious-metal catalyst at atmospheric or higher pressures and at 800–950 °C. The overall reaction is: $NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$ + 98.7 kcal [413.2 kJ] evolved. The concentration of nitric acid produced with conventional equipment is usually about 60%; if higher concentrations are desired, special equipment or processes are required. Typical processes used for nitric acid manufacture have included low-pressure (800 °C; atmospheric pressure; 50–52% acid strength); medium-pressure (Montecatini process: 850 °C; 40 psi [276 kPa]; 60% acid strength); medium-pressure (Kuhlman process: 850 °C; 40 psi; 70% acid strength); high-pressure (DuPont process: 950 °C; 120 psi [827 kPa]; 60% acid strength); and Pintsch Bamag's 'Hoko Process' (850 °C; atmospheric pressure; 98–99% acid strength) (Green, 1974; Green & Li, 1983).

The first processes for oxidation of ammonia operated at atmospheric pressure. Both high-pressure and dual-pressure processes have been used, but the latter is widely used today. In this process, ammonia is oxidized at 72.5 psi [500 kPa], and the oxidation products are absorbed at 160 psi [1 MPa]. The low pressure used for oxidation promotes high conversion efficiency and minimizes losses of the precious-metal catalyst (Green & Li, 1983).

Nitric acid is produced by the standard ammonia–oxidation processes as an aqueous solution at a concentration of 50–70 wt%. Such concentrations are suitable for the production of ammonium nitrate, but anhydrous nitric acid is required for use in organic nitrations. Since nitric acid forms an azeotrope with water at 68.8 wt%, water cannot be separated from the acid by simple distillation. Two industrial methods for concentrating nitric acid are extractive distillation and reactions with additional nitrogen oxides; these latter reactions are the direct, strong nitric processes (Newman, 1981).

Extractive distillation is the most widely used method for concentrating nitric acid. It consists of mixing 60% nitric acid with strong (93%) sulfuric acid and passing the mixture through a distillation system from which concentrated (95–98%) nitric acid and denitrated, residual sulfuric acid containing approximately 70% H_2SO_4 are obtained. The dilute, residual sulfuric acid may be reconcentrated for further use. In the Pintsch Bamag process, nitric acid is concentrated on the basis of the difference in the composition of the nitric acid–water constant boiling mixtures at different pressures in a two-column distillation system (Green & Li, 1983).

Modifications of a concentration process that was described in 1932, direct, strong nitric processes, have been widely used in Europe. Nitrogen tetroxide is separated from the process gases that leave the ammonia converter by refrigeration or by absorption in concentrated nitric acid. The tetroxide then reacts with weak nitric acid and air or oxygen to yield a 98 wt% product (Newman, 1981).

Worldwide production of nitric acid is presented in Table 5. White fuming nitric acid usually contains 90–99 wt% nitric acid, 0–2 wt% nitrogen dioxide and up to 10 wt% water. Red fuming nitric acid usually contains about 70–90 wt% nitric acid, 2–25 wt% nitrogen dioxide and up to 10 wt% water. Over time, concentrated nitric acids tend to decompose to nitrogen dioxide, water and oxygen; as a result, pressure builds up in storage vessels. Decomposition of concentrated acid is reduced by adding such substances as quaternary ammonium compounds, organic sulfones, inorganic persulfates and organic sulfonium compounds. Nitric acid is also very corrosive, and stabilizers and corrosion inhibitors are sometimes used; for instance, corrosion of aluminium by red fuming nitric acid is reduced by adding 4 wt% of hydrogen fluoride (52% HF) (Green, 1974; Green & Li, 1983).

1.2.7 *Phosphate fertilizer manufacture*

The phosphate minerals fluorapatite [$3Ca_3(PO_4)_2 \cdot CaF_2$] and hydroxyapatite [$3Ca_3(PO_4)_2 \cdot Ca(OH)_2$] (Hudson & Dolan, 1982) supply the bulk of the phosphorus in

Table 5. Trends in production of nitric acid in some countries (thousand tonnes)

Country	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
Brazil	381.0	349.0	308.0	321.1	355.6	364.8	389.8	407.6	387.5	NR	NR
Canada	712.6	1157.7	976.8	1060.8	1100.5	1128.3	1023.9	899.9	919.3	1026.6	965.0
China	227.6	184.4	246.1	255.9	257.7	273.9	275.3	290.2	302.1	NR	NR
Germany[a]	3172.4	2883.0	2286.1	2620.9	2850.4	2885.3	2816.8	2639.0	2312.4	2180.4	1879.7
India	454.0	561.0	487.0	551.0	529.0	NR	NR	NR	NR	NR	NR
Italy	1011.5	1005.5	1029.7	1027.8	1099.9	1181.5	1091.6	1195.2	1193.3	1108.1	1040.1
Japan	NR	470.7	531.1	540.0	581.0	578.4	563.4	573.0	618.0	NR	NR
Mexico	170.0	161.0	167.0	167.0	171.0	173.0	154.0	NR	NR	NR	NR
Spain	1266.4	1225.9	1199.5	1054.7	1285.0	1245.8	1292.9	1211.0	1247.8	1266.9	NR
United Kingdom	NR	2973.2	3083.8	3144.8	NR	NR	NR	NR	2364.9	NR	NR
USA	8374.2	8249.0	6704.1	6139.8	7008.9	6922.7	6109.0	6554.4	7249.3	7574.1	7029.8

From Anon. (1983, 1987, 1991); Dialog Information Services (1991); NR, not reported

[a] Data are for western Germany only.

fertilizers manufactured all over the world. The powdered rock itself is useless as a fertilizer, however, because the phosphorus it contains is not water-soluble and thus not readily available to plants. Reacting the rock with sulfuric, nitric or hydrochloric acid produces phosphoric acid (H_3PO_4) and superphosphoric acid—important intermediates in the production of phosphate fertilizers (United Nations Industrial Development Organization, 1978; Fertilizer Institute, 1982).

The oldest commercial fertilizer is normal superphosphate (containing 19–20% phosphorus as P_2O_5), first made in about 1840. This was the leading phosphate fertilizer for many years, but by the 1970s it had been supplanted to a large extent by ammonium phosphates and triple superphosphate. One reason for its long tenure is the ease with which it can be manufactured: All that is necessary is to mix pulverized phosphate rock with sulfuric acid, wait until the mixture sets into a solid and cures (completes the reaction), and then break up the mass. About half of the normal weight of superphosphates is gypsum (calcium sulfate) (Fertilizer Institute, 1982).

By using a higher ratio of sulfuric acid to phosphate rock, phosphoric acid (52–54% phosphorus as P_2O_5) rather than normal superphosphate can be produced. The crude product contains phosphoric acid with solid calcium sulfate in suspension. The calcium sulfate is separated by filtration, giving a large quantity of waste by-product (nearly 5 tonnes per tonne of P_2O_5 in phosphoric acid). Phosphoric acid (H_3PO_4) made in this way is called 'wet-process' acid. The acid is concentrated by evaporation to the usual commercial grade of 52–54% P_2O_5. It is used in making triple superphosphate, ammonium phosphate and liquid mixed fertilizers. 'Furnace'-grade phosphoric acid is made by smelting phosphate rock with coke and silica in an electric furnace. The elemental phosphorus produced is burned and converted to phosphoric acid. This relatively pure acid is now used almost entirely in the detergent and food industries, as the high production cost essentially eliminated use of 'furnace' acid in the production of commercial fertilizers by the early 1970s (Fertilizer Institute, 1982).

Superphosphoric acid (68–72% phosphorus as P_2O_5) (Herrick, 1982) is made by concentrating wet-process acid past the point needed for the usual 52–54% P_2O_5 grade. The composition of superphosphoric acid differs radically from that of ordinary phosphoric acid: It contains mainly polyphosphates rather than orthophosphate. It is a fluid at ordinary temperature, even though there is little or no water present, and this property confers certain advantages—higher solubility and readier solubilization of impurities when it is used to make fluid fertilizers. Polyphosphates in superphosphoric acid became the backbone of high-quality liquid fertilizers in the 1960s and 1970s (Fertilizer Institute, 1982).

When phosphate rock is treated with phosphoric acid, triple superphosphate (44–51% phosphorus as P_2O_5) results (Herrick, 1982). The operation is similar to that for making normal superphosphate, but the product has more than twice the P_2O_5 content because phosphoric acid is used rather than sulfuric acid. It is produced in granular and nongranular forms. Triple superphosphate is second to ammonium phosphates in use among phosphate fertilizers worldwide (Fertilizer Institute, 1982).

Phosphoric acid treated with ammonia produces ammonium phosphates. The high nitrogen and phosphorus content, high water solubility, good physical characteristics and low production costs of granular ammonium phosphates have made these compounds the leading fertilizers in the world. The most popular type is diammonium phosphate (18% nitrogen and 46% phosphorus as P_2O_5), which is made in very large plants and used widely in bulk blending. Other types are monoammonium phosphate, produced with various ratios of nitrogen and phosphorus, and ammonium phosphate plus ammonium sulfate, typically containing 16% nitrogen and 20% phosphorus as P_2O_5. Monoammonium phosphate is also produced in nongranular form and used in the production of granular nitrogen–phosphorus–potassium and suspension fertilizers (Fertilizer Institute, 1982).

Worldwide production of phosphate fertilizers is presented in Table 6.

Table 6. Regional phosphate fertilizer production (thousand tonnes)

Region	1960	1965	1970	1975	1980	1985	1987
North America	2736	3991	5451	7229	9786	10321	8613
Western Europe	3839	4825	5579	6275	5574	4812	4133
Eastern Europe	553	1209	1909	2641	3207	3165	3096
USSR	879	1407	2072	3504	5083	6330	7687
Oceania	728	1140	1134	1029	1330	870	830
Africa	244	377	742	956	1103	1573	1771
Latin America	91	183	328	769	1510	1714	1921
Asia	705	1466	2237	3432	4634	6832	7503

From Bumb (1989)

1.2.8 *Lead battery (accumulator) manufacture*

In 1860, Gaston Planté presented the first working model of the lead–acid secondary battery to the French Academy of Science. Lead–acid batteries, or accumulators, are used to store electrical energy. The basic components of a lead–acid battery are the container (case, cover and vent plugs) and the cell; the cell contains the plates (positive, lead dioxide on lead grid; negative, lead on lead grid), separators and electrolyte solution (approx. 33 wt% aqueous H_2SO_4). There are three principal categories of lead–acid battery: *automotive* (for cranking internal combustion engines); *industrial or stationary* (heavy-duty applications, such as motive power, and stand-by power for vital facilities, such as power stations, telephone exchanges and hospitals); and *consumer* (emergency lighting and security systems, cordless appliances and tools and small engine starting) (Doe, 1978; Sander *et al.*, 1984; Berndt, 1985).

A lead–acid battery may contain any number of cells, depending on the voltage: Stationary batteries contain up to 120 cells (240 volts), whereas automobile batteries generally contain three or six cells (6 or 12 volts). Lead–acid storage batteries vary in size and weight (100 g to several tonnes), depending on the capacity required (US Environmental Protection Agency, 1989a).

The manufacture of lead–acid batteries has been described in detail by Hehner (1986). Battery manufacture begins with grid casting and paste mixing. Two grids are generally cast at the same time from molten lead, to which calcium (0.1%), antimony (2.5–6.0%), arsenic (see IARC, 1987) (0.3–0.6%) or tin (0.1–0.6%) is added as an alloy component. These grids are coated with either positive or negative paste, formed, cured, cut into two (a process called slitting) and then sent to be assembled (Hehner, 1986; US Environmental Protection Agency, 1989a).

The paste mixing operation is a batch-type process in which lead oxide is added to the mixer, water and sulfuric acid are added, and the mixture is blended to form a stiff paste. Approximately 1 wt% of expander (generally a mixture of barium sulfate, carbon black (see IARC, 1987) and organic compounds) is added to batches of paste to make negative plates. The paste is then applied to the grids, which are flash dried and then stacked and sent to curing ovens. After the plates have been cured, they are sent to the three-process operation, which includes plate stacking, welding and assembly of elements into the battery case (US Environmental Protection Agency, 1989a).

During formation, the inactive lead oxide–sulfate paste is converted chemically into an active electrode. Formation is essentially an oxidation–reduction reaction, in which the lead oxide in the positive plates is oxidized to lead dioxide (PbO_2) and that in the negative plates is reduced to metallic lead. This is accomplished by placing the unformed plates in a dilute (10–25%) sulfuric acid solution and connecting the positive plates to the positive pole and the negative plates to the negative pole of the direct current source. During the formation process, hydrogen is released in the form of small bubbles, which carry sulfuric acid with them as they break through the surface of the solution and enter the atmosphere above the container. The emissions of sulfuric acid mist generally increase with increasing temperature and rate of charge; and, as the formation cycle nears the end, the release of hydrogen bubbles increases, augmenting emissions of sulfuric acid (US Environmental Protection Agency, 1989a).

In the manufacture of lead–acid batteries using the wet ('jar') formation process, the elements are assembled in the case before forming. It is common practice to place the cells in the battery case, put the lid on the battery and add sulfuric acid. After formation, additional acid is added to fill the battery completely or the spent acid is dumped from the battery and new acid is added. Wet formation generally takes one to four days. In most plants, a 36- to 48-h forming cycle is used; the charging rate is high during the first 24–36 h and lower during the remaining 12 h (US Environmental Protection Agency, 1989a).

The dry ('tank') formation process can be performed in several ways. In some cases, the plates are formed individually in tanks of sulfuric acid and then assembled. Most often, however, the plates are assembled into elements before formation, and these elements are placed in large tanks of sulfuric acid and connected electrically. Dry formation typically lasts 16 h, plates or elements being loaded into tanks during the day shift and formed during the evening and night shifts (US Environmental Protection Agency, 1989a).

Global shipments of automotive batteries in 1990 amounted to 233.8 million units: 84.9 million units for North America; 67.3 million units for Europe; 53.7 million units for Asia and the Pacific; 17.9 million units for Latin America; and 10.0 million units for Africa and the Middle East (Ficker, 1991).

1.3 Analysis

Methods for the measurement and analysis of strong acids in atmospheric samples have been reviewed. These include thermal volatilization, extraction with pH measurement or proton titration, specific extraction of atmospheric acids, specific extraction with derivatization and continuous and/or real-time analysis using flame photometric detection (Tanner, 1987).

1.4 Exposures in the workplace

In this section, occupational exposures to mists, vapours and gases of sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid in various industries and occupations are summarized. Table 7 lists industries in which exposures to these acids may occur. Most of the sulfuric acid consumed in the USA is in phosphate fertilizer production, where it is used to convert phosphate rock to phosphoric acid. Other industrial uses include production of pigments, textiles (see IARC, 1990b), explosives, alcohols and detergents, petrochemical refining and chemical manufacturing, plating and pickling of metals and lead–acid battery production. Nitric acid is used primarily in making synthetic fertilizers and in explosives, plastics, fibres, dyestuffs and other chemical manufacturing industries. Most of the hydrochloric acid produced in the USA is used within the chemical industry in oxyhydrochlorination processes, e.g., making vinyl chloride and chlorinated solvents. Hydrochloric acid is also produced as a by-product in the manufacture of vinyl chloride (see IARC, 1987), chlorinated ethanes and ethylenes, fluorocarbons and other chlorinated organics, and isocyanates. Phosphoric acid is used primarily in phosphate fertilizer production, with additional consumption for the production of detergents, animal feed supplements, metal treatment agents, water softeners and fire retardants.

A list of occupations in which workers may be exposed to strong inorganic acids is presented in Table 8. Very few data exist on the numbers of workers exposed. In the USA, the National Occupational Exposure Survey conducted by the National Institute for Occupational Safety and Health between 1981 and 1983 provided estimates of the numbers of US workers with potential exposure to sulfuric (776 000), hydrochloric (1 239 000), nitric (298 000) and phosphoric (1 257 000) acids (US National Institute for Occupational Safety and Health, 1990). The occupations listed and the estimates of numbers of workers were based on a survey of US companies and did not involve measurements of actual exposures.

The following sections address eight industries in which exposures to acid mists, vapours and gases occur. Exposures in each of these industries are described, and mechanisms by which acid mists, vapours and gases may be generated are given when that information was available for specific processes. In general, the factors that affect generation of gases and vapours include temperature and pressure; additional factors that influence the generation of vapours from solutions are solution strength and evaporative surface area. Mists may be formed by either condensation of vapour or disturbance of liquid solutions, such as release of dissolved gases or mechanical agitation. Occupational exposures also depend on the proximity of a worker to sources of mists and vapours and on process control measures such as ventilation and containment.

1.4.1 *Isopropanol manufacture*

No measurement has been published of exposure to sulfuric acid in isopropanol plants. Potential exposures include propylene and sulfuric acid (raw materials), diisopropyl and isopropyl hydrogen sulfates (intermediates), isopropanol (product), isopropyl ether and

Table 7. Industries in which there is potential exposure to strong inorganic acids

Industry	Sulfuric acid	Hydrochloric acid	Nitric acid	Phosphoric acid
Aerospace		+	+	
Building and construction	+	+	+	+
Chemical manufacture	+	+	+	+
– isopropanol	+			
– sulfuric acid	+			
– synthetic ethanol	+			
– vinyl chloride		+		
Detergents	+			
Electric and electronic equipment	+	+	+	+
Fertilizers	+		+	+
Food products	+	+	+	+
Health services	+	+	+	+
Instruments	+	+	+	+
Lead–acid batteries	+			
Leather	+	+	+	+
Metal plating	+	+	+	+
Metal cleaning and pickling	+	+	+	+
Metal extraction and ore processing	+	+	+	+
Oil and gas extraction	+	+		+
Petroleum and coal products	+	+	+	+
Photography shops	+	+	+	+
Printing and publishing	+	+	+	+
Paper and allied products	+	+	+	+
Rubber and plastic products	+	+		+
Semiconductors		+	+	
Soap	+			
Steel	+	+	+	
Textile products	+	+	+	+
Zinc galvanizing		+		

From US National Institute for Occupational Safety and Health (1974, 1976); Burgess (1981); Soule (1982); US National Institute for Occupational Safety and Health (1990)

isopropyl oil (by-products), and benzene (process chemical) (see section 1.2.1). According to veteran employees of a plant in the USA where synthetic ethanol was produced from 1930 to 1968 and isopropanol from 1928 to 1949 by the strong-acid method, the process was initially poorly controlled, and misting of sulfuric acid and other agents took place during the opening of reaction vessels; later, the process was operated from a well-ventilated remote-control office (Teta *et al.*, 1992). Maximal air concentrations of diisopropyl sulfate over a spill in the USA have been calculated (Lynch *et al.*, 1979; see the monograph on diisopropyl sulfate, section 1.3.2).

Table 8. Occupations in which there is potential exposure to strong inorganic acids

Occupation	Sulfuric acid	Hydrochloric acid	Nitric acid	Phosphoric acid
Alloy workers	+	+	+	
Anodizers	+	+	+	+
Artists	+	+	+	
Battery workers	+			
Cement workers		+		
Chemical workers	+	+	+	+
Chemists	+	+	+	+
Coke production	+	+	+	+
Corn millers	+			+
Crane operators	+	+	+	+
Detergent manufacturers	+			
Dyers		+	+	
Electroplaters	+	+	+	+
Electrowinners		+	+	
Explosives manufacturers			+	
Firefighters		+		
Fertilizer processors	+		+	+
Jewellers		+	+	
Laboratory workers	+	+	+	+
Leather manufacturers	+	+	+	+
Maintenance workers	+	+	+	+
Metal cleaners, picklers, cranemen	+	+	+	+
Metal workers	+	+	+	+
Oil workers	+	+		
Paper mill workers	+	+	+	+
Petrochemical workers	+	+	+	+
Photography lab workers	+	+	+	+
Platers	+	+	+	+
Printing machine operators	+	+	+	+
Refinery operators	+	+	+	
Soap manufacturers	+			
Sheet metal workers	+	+	+	
Steel workers	+	+	+	
Textile workers	+	+	+	+
Toll-booth workers	+		+	
Wire millers		+	+	
Zinc die casters	+	+	+	+

From Burgess (1981); Soule (1982); US National Institute for Occupational Safety and Health (1990)

1.4.2 *Synthetic ethanol manufacture*

No measurements of exposure to sulfuric acid in synthetic ethanol plants have been published. Potential exposures include ethylene and sulfuric acid (raw materials), diethyl and ethyl hydrogen sulfates (intermediates), ethanol (product), diethyl ether (by-product), phosphoric acid (catalyst) and benzene, cyclohexane or ethylene glycol (process chemicals) (see section 1.2.1). According to interviews with supervisors at a synthetic ethanol plant in the USA, there is opportunity for exposure to acid mist in the general plant area and particularly in operations involving vat-type acid coolers operated in an open mode. Exposure to diethyl sulfate is also possible, e.g., during pump seal leakages and maintenance and cleaning of absorbers and extract soakers. Maximal air concentrations of diethyl sulfate over a spill have been calculated (Lynch *et al.*, 1979; see the monograph on diethyl sulfate, section 1.3.2).

1.4.3 *Pickling and other acid treatment of metals*

Most of the data on occupational exposures to acid aerosols have been obtained in the plating and pickling industries; in general, these data represent the highest measured exposures. These data are summarized in Table 9. Sulfuric, hydrochloric, nitric and phosphoric acids are all used in pickling processes. Phosphoric acid use is generally limited to pickling, chemical polishing and phosphate conversion coatings. Sulfuric, hydrochloric and nitric acids are also used for electroplating. Plating processes that involve one of these acids include decorative (bright) and hard chromium, nickel, copper, tin and platinum plating.

(*a*) *Pickling, cleaning, etching*

Arithmetic means of the concentrations of sulfuric acid in the air during pickling and acid cleaning ranged from < 0.01 to 5.6 mg/m^3.

Arithmetic mean concentrations of hydrochloric acid in the air of Finnish and US plants ranged from < 0.2 to 13.6 mg/m^3; in a study in China, a mean value of 59 mg/m^3 was observed (Xu & Zhang, 1985). Individual measurements of hydrochloric acid in air ranged from 0.2 to 49.8 in French (Lamant *et al.*, 1989), German (Mappes, 1980) and Russian (Muravyeva *et al.*, 1987) studies. Geometric mean air concentrations of hydrochloric acid at six sites in a Dutch zinc galvanizing plant were 1.8–12.4 mg/m^3; the estimated arithmetic means (assuming a lognormal distribution) were approximately 2.3–15 mg/m^3 (Remijn *et al.*, 1982).

Few measurements are available of exposure to nitric acid; individual concentrations in air are 0.01–0.4 mg/m^3. The concentrations of phosphoric acid in air were measured in three studies: $\leq$ 0.04 mg/m^3 (Ruhe & Donohue, 1980), < 0.67 mg/m^3 (Daniels & Orris, 1981) and 0.03 mg/m^3 (Geissert, 1977).

Other exposures that may occur during acid cleaning of metals are to chromic acid, chromates, hydrogen fluoride, sodium fluoride, sodium hydroxide and alkaline salts. In an evaluation by the US National Institute for Occupational Safety and Health of health hazards in one steel manufacturing facility in the USA, detectable quantities of iron oxide (average, 0.8 mg/m^3; range, 0.34–2.7 mg/m^3) and lead (average, 0.04 mg/m^3; range, none detected to 0.27 mg/m^3) were measured in 14 full-shift personal samples (Price, 1977). Copper, manganese, chromium, zirconium, hafnium, respirable free silica, phenol and formaldehyde were not detected.

Table 9. Occupational exposures to strong inorganic acid mists and vapours during acid treatment of metals

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
					Mean	Range			
Pickling									
Batch	H_2SO_4	Surface treatment	NR	2	5.6	0.7–10.5	1957, 1966	Finland	FIOH (1990)
Pickle hooker		Steel	Personal	7	0.15	0.07–0.25	1975	USA	Beaumont *et al.* (1987)
Ass't pickle hooker			Personal	4	0.20	< 0.03–0.48			
Crane operator			Personal	4	0.22	0.15–0.29			
		Wire manufacture (cleaning department)	Personal	20	0.22	< 0.01–0.64	1976–77	USA	Haas & Geissert (1977)
Pickle tanks		Steel	Area	2	0.15	0.12–0.27	1977	USA	Beaumont *et al.* (1987)
Crane operator			Area	10	0.25	0.01–0.50			
		Steel	Personal	6	0.15	0.09–0.19	1977	USA	Price (1977)
			Area	2	0.20	0.12–0.27			
Crane operator		Steel and alloy wire mill	Area	8	0.29	0.13–0.50	1977	USA	Geissert (1977)
Crane cab and catwalk			Area	13	0.68	0.11–2.94			
Cold finishing		Steel rod and wire mill	Area	3	0.032	0.016–0.05	1979	USA	Young (1979a)
		Seamless steel tubing manufacture	Personal full shift	13	0.17	0.08–0.47	1980	USA	Daniels & Orris (1981)
			Personal short term	6	NR	< 0.67–0.97	1981	USA	
		Radio tower manufacture	Personal	13	0.11	0.05–0.18	1981	USA	Kominsky (1981a)
			Area	5	2.97	1.05–5.66			
Milling area near pickling area		Steel	Personal	4	< 0.1		1986	USA	Ahrenholz (1987)
			Area	4	< 0.1				
Continuous		Steel	Personal	8	0.1	< 0.01–0.16	1977	USA	Anania *et al.* (1978)
			Area	2	0.05	< 0.01–0.09			
Crane operator			Area	2	0.1	0.09–0.14			
			Personal	2	0.16	NR			
Cold strip mill		Nonfabricated steel	Area	3	0.92	0.35–1.20	1979	USA	Young (1979b)
Finishing			Area	2	0.09	0.039–0.14			

Table 9 (contd)

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
					Mean	Range			
Pickling (contd)									
Batch	HCl	Zinc galvanizing	Personal	51	5.3^a	2.09^b	1978–82	Netherlands	Remijn *et al.* (1982)
				50	4.1^a	2.00^b			
				51	2.3^a	1.82^b			
				52	1.8^a	2.00^b			
				47	3.4^a	2.29^b			
				52	12.4^a	1.82^b			
Crane cab		Steel and alloy wire mill	Area	12	0.4	< 0.004–2.72	1977	USA	Geissert (1977)
Crane cab detector tubes			Personal	4	1.0	0.5–1.5			
Continuous		Welding wire	Area	2	0.15	0.1–0.2	1979	USA	Lee (1980)
		Steel	NR	10	59	5–175	NR	China	Xu & Zhang (1985)
'Acid pickling'		Surface treatment	NR	2	5.66	4.47–6.7	1952–67	Finland	FIOH (1990)
'Pickling'		Steel	NR	3	29.2	26.5–33.5	1980	Germany	Mappes (1980)
				4	3.73	1.7–5.2			
				8	5.74	3.8–8.4			
				6	2.05	0.8–4.5			
'Pickling'		Galvanization	NR	NR		1.36–6.88	NR	France	Lamant *et al.* (1989)
Milling area near pickling area		Steel	Personal	4	< 0.2		1986	USA	Ahrenholz (1987)
			Area	4	< 0.2				
Batch									
Short term	H_3PO_4	Steel	Personal	NR	< 0.67		1981	USA	Daniels & Orris (1981)
Cab and catwalk		Steel and alloy wire mill	Area	3	0.03	0.02–0.05	1977	USA	Geissert (1977)

Table 9 (contd)

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
					Mean	Range			
Cleaning									
	H_2SO_4	Coin manufacture	NR	2	0.8	0.3–1.2	1952	Finland	FIOH (1990)
		Metal processing	NR	3	1.7	0.6–3.2	1960	Finland	FIOH (1990)
		Metalware manufacture	NR	2	0.2	ND–0.3	1974, 1975	Finland	Skyttä (1978)
		Aircraft manufacture	Area	3	< 0.015		1977	USA	Hervin *et al.* (1977)
		Small electronic parts	Area	1	0.01		1980	USA	Sheehy *et al.* (1982a)
		Semiconductors	Area	1	< 0.01		1981	USA	Gunter (1982)
Strip acid, enclosed process, ventilation		Steel	Area	48	0.333	< 0.248– > 1.205	NR	Wales (UK)	Anfield & Warner (1968)
Small steel components		Automobile manufacture	Area	85	2.96	< 0.360– > 14.43	NR		
	HCl	Surface treatment	NR	2	1.79	1.34–2.1	1952–67	Finland	FIOH (1990)
		Small electronic parts	Area	2	0.25	0.22–0.28	1980	USA	Sheehy *et al.* (1982a)
Continuous	HCl	Continuous coiled steel galvanizing	Personal	9	0.23	0.16–0.29	1981	USA	Kominsky (1981b)
Attendant's desk			Area	1	0.27				
Crane cab			Area	7	0.87	0.48–2.20			
		Semiconductors	Area	2	< 0.25		1981	USA	Gunter (1982)
	HNO_3	Small metal components	Area	2	0.021	0.014–0.027	1975–76	USA	Geissert (1976)
		Small electronic parts	Area	NR	0.03		1980	USA	Sheehy *et al.* (1982a)
		Semiconductors	Personal	4	0.12	ND–0.4	1983	USA	Moseley (1983)
Chromic acid stripping	H_3PO_4	Automobile trim	Personal	2	< 0.01		1976	USA	Ruhe & Andersen (1977)

Table 9 (contd)

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
					Mean	Range			
Etching									
	H_2SO_4	Aircraft maintenance	Personal	3	0.067	< 0.047–0.106	1981	USA	Godbey (1982)
			Area	4	0.062	0.053–0.083			
	HCl	Galvanizing	NR	NR	4.14	0.2–49.8	NR	USSR	Muravyeva *et al.* (1987)
Titanium		Aircraft manufacture	Area	4	0.1	NR	1977	USA	Hervin *et al.* (1977)
Titanium	HNO_3		Area	8	0.10	0.01–0.30			
Aluminium			Area	6	0.027	0.01–0.05			
		Semiconductors	Personal	7	0.03	ND–0.2	1983	USA	Moseley (1983)
Electrolytic refining									
Tank house	H_2SO_4	Secondary copper smelting and refining	Personal	4	0.072	0.056–0.097	1982–83	USA	Kominsky & Cherniack (1984)
			Area	2	0.043	0.031–0.055			
Millwright			Personal	3	0.114	0.065–0.191			
Tank house			Personal	4	0.13	0.083–0.265	1978	USA	Kominsky & Kreiss (1981)
			Area	1	0.042				
Electrowinning		Copper cathode	Personal	12	0.27	0.02–0.79	1978	USA	Ruhe & Donohue (1980)
			Area	4	0.21	0.08–0.35			
Electrowinning cell house		Zinc plant	NR	NR	NR	0.5–1.0	1977	Finland	Roto (1980)
Sulfatizing, roasting		Cobalt plant	NR	4	5.6	3.3–8.2	1968	Finland	FIOH (1990)
Dissolving			NR	4	0.93	0.5–1.6			
Electrolysis	H_2SO_4	Metal processing	NR	8	0.3	0.2–0.4	1960	Finland	FIOH (1990)
		Nickel manufacture	NR	11	0.6	0.2–1.2	1966	Finland	FIOH (1990)
		Metal manufacture	NR	2	1.3	1.2–1.4	1972–73	Finland	Skyttä (1978)
Incineration		Secondary silver smelting and refining	Area	2	0.01	NR	1981	USA	Apol (1981a)
Slag removal	HCl	Cable manufacture	NR	1	3		1972	Finland	Skyttä (1978)
Refining	HNO_3	Secondary silver smelting and refining	Personal	2	0.41	NR	1981	USA	Apol (1981a)
			Area	2	0.39	0.36–0.41			

Table 9 (contd)

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
					Mean	Range			
Plating									
	H_2SO_4	Electronic instrument	Personal	2	0.14	0.02–0.26	1975–76	USA	Ruhe (1976)
		Aerospace component	Personal	3	< 0.09		1978	USA	Evans (1978)
		Small electronic parts	Area	4	0.12	0.04–0.23	1980	USA	Sheehy *et al.* (1982a)
		Chrome plating	Personal	6	< 0.04	< 0.04–< 0.05	1980	USA	Sheehy *et al.* (1982b)
			Area	1	0.06				
Over liquid			Area	3	< 0.05	SD, 0.01			
On tank perimeter			Area	6	1.7	SD, 1.87			
Before ventilation			Area	2	7.3	NR			
After ventilation			Area	2	4.4	NR			
Mixed acid bath			Area	6	5.15	0.74–11.84			
		Hard chrome plating	Personal	8	0.2	< 0.2–0.4	1981	USA	Sheehy *et al.* (1982c)
			Area	12	0.4	0.2–0.7			
			Area	6	0.4	0.3–0.5			
			Area	15	0.4	0.2–0.8			
			Personal	5	0.11	0.10–0.12	1981	USA	Mortimer *et al.* (1982)
			Area	15	< 0.11	< 0.11–0.15			
			Area	3	0.013	0.010–0.015	1981	USA	Ahrenholz & Anderson (1981)
Electroplating		Galvanizing	NR	NR	1.8	NR	NR	USSR	Kuprin *et al.* (1986)
Cadmium covering			NR	NR	0.58	0.08–1.33	NR	USSR	Muravyeva *et al.* (1987)
Copper covering			NR	NR	0.47	0.05–0.7	NR		
Tin-bismuth covering			NR	NR	0.74	0.01–2.33	NR		
Copper coating		Welding wire	Area	2	0.05	ND–0.1	1979	USA	Lee (1980)
Plating tank		Hard chrome plating	Area	10	0.48	0.17–1.4	1981	USA	Spottswood *et al.* (1983)
				8	0.30	0.13–0.36			
				15	0.38	0.21–0.60			
				23	0.82	0.53–1.28			
				12	0.12	NR			

Table 9 (contd)

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
					Mean	Range			
Plating (contd)									
General area			Area	4	0.18	0.15–0.27			
				2	0.10	NR			
			Personal	4	0.433	0.109–0.903			
				4	0.421	0.107–0.967			
				2	0.128	0.110–0.145			
		Fishing rod component	Personal	1	< 0.06		1986	USA	Daniels & Gunter (1987)
			Area	3	< 0.19				
	HCl	Electronic instrument	Personal	4	0.30	0.001–0.48	1975–76	USA	Ruhe (1976)
			Area	1	0.15				
Bright dip tank		Small electronic parts	Area	6	0.14	< 0.006–0.54	1980	USA	Sheehy *et al.* (1982a)
		Fishing rod component	Personal	1	< 0.06		1986	USA	Daniels & Gunter (1987)
Zinc coating	HCl	Surface treatment	NR	3	7.45	3.58–14.5	1952–67	Finland	FIOH (1990)
Tin coating			NR	1	0.75				
Cadmium coating			NR	1	0.75				
	HNO_3	Aerospace component	Personal	9	0.034	0.01–0.13	1978	USA	Evans (1978)
Before ventilation		Chrome plating	Area	2	0.76		1980	USA	Sheehy *et al.* (1982b)
After ventilation			Area	2	0.48				
Nitric acid bath			Area	6	1.3	0.05–2.8			
Mixed acid bath			Area	17	0.97	0.05–2.76			
			Personal	5	0.26	< 0.04–0.64			
Bright dip tank		Small electronic parts	Area	6	0.05	0.03–0.10	1980	USA	Sheehy *et al.* (1982a)
Anodizing	H_2SO_4	Aluminium galvanizing	NR	NR	0.65	0.05–2.1	NR	USSR	Muravyeva *et al.* (1987)
		Automobile trim	Personal	2	< 0.01		1976	USA	Ruhe & Andersen (1977)
	HCl	Aircraft component	Personal	3	0.09	0.03–0.2	1976	USA	Gunter (1976)
	HNO_3	Aircraft component	Personal	3	0.03	0.01–0.04			
	HNO_3	Automobile trim	Personal	3	0.05	0.02–0.10	1976	USA	Ruhe & Andersen (1977)

Table 9 (contd)

Operation	Acid	Industry	Sample type	No. of samples	Air concentration (mg/m³)		Year of measurement	Country	Reference
					Mean	Range			
Miscellaneous									
Acid recovery	H_2SO_4	Steel	Area	42	0.795	< 0.227–2.626	NR	Wales (UK)	Anfield & Warner (1968)
Dip		Copper pipe	Personal	5	0.06	< 0.05–0.17	1974	USA	Gunter & Bodner (1974)
Hydrolysis		Ferrovanadium	Area	NR	4.7	2.0–7.5	NR	USSR	Kazimov (1977)
Electrochemical drilling		Jet engine components	Personal	17	0.09	< 0.1–1.27	1975	USA	Kominsky (1975)
			Area	4	< 0.1				
Photo-resist		Semiconductors	Area	4	0.03	< 0.01–0.11	1981	USA	Gunter (1981)
Aluminium finishing		Custom finishing	Personal	7	0.10	0.04–0.19	1979	USA	Ruhe & Donohue (1980)
			Area	1	0.11				
Acid testing office		Steel sheet and tin plate	Area	1	0.026		1979	USA	Young *et al.* (1979)
Surface treatment		Metalware	NR	11	0.3	0.01–0.7	1971–76	Finland	Skyttä (1978)
Electrochemical drilling	HCl	Jet engine component	Area	1	0.83		1975	USA	Kominsky (1981a)
			Personal	2	0.06	0.03–0.09			
Leaching		Titanium sponge model	Area	2	0.31	0.15–0.47	1978	USA	Moseley *et al.* (1980)
Lighting		Galvanization	NR	NR	1.03	0.66–2.3	NR	USSR	Muravyeva *et al.* (1987)
Sintering		Steel	NR	8	ND		1955	Finland	FIOH (1990)
Opening of oven		Metalware	NR	2	13.6	9.4–17.9	1975	Finland	Skyttä (1978)
Surface treatment			NR	4	1.55	0.5–3.4	1971, 1975		
Diffusion	HNO_3	Semiconductors	Personal	8	0.01	ND–0.03	1983	USA	Moseley (1983)
Aluminium finishing		Custom finishing	Personal	7	0.046	0.02–0.15	1979		Ruhe & Donohue (1980)
			Area	1	0.06				
Surface treatment		Metalware	NR	1	0.3		1971	Finland	Skyttä (1978)
Aluminium finishing	H_3PO_4	Custom finishing	Personal	7	0.01	< 0.003–0.04	1979	USA	Ruhe & Donohue (1980)
			Area	1	0.04				

ND, not detected; NR, not reported

[a]Geometric mean

[b]Geometric standard deviation

(*b*) *Electrolytic refining*

Mean exposures to sulfuric acid during electrolytic refining were 0.01–5.6 mg/m^3. Other exposures in smelters and in the secondary metals industry are to arsenic, sulfur dioxide, cadmium and other metal dusts (Kaminsky & Cherniack, 1984).

(*c*) *Plating and anodizing*

During chromium plating in US facilities, the mean concentrations of sulfuric acid in air ranged from 0.01 to 7.3 mg/m^3. Information on exposure during anodizing is limited; however, the air concentrations of nitric, hydrochloric and sulfuric acids appear to be lower than during plating. Other exposures in plating and anodizing processes may be to hydrogen fluoride, ammonium chloride, zinc chloride, zinc oxide, sulfurous anhydride, nitrogen oxides, chromic acid, hydrogen cyanide, alkaline salts, alkaline mists, metal salts and metal dusts, depending on the process (Soule, 1982; Lamant *et al.*, 1989).

1.4.4 *Sulfuric acid manufacture*

In a sulfuric acid plant in Sweden, area samples taken in 1979–80 contained sulfuric acid at 0.1–3.1 mg/m^3; breathing zone samples contained < 0.1–2.9 mg/m^3. Sulfur dioxide concentrations measured in 1969–84 ranged from 2.4 to 124 mg/m^3 in area samples (mean, 9.1 mg/m^3) and 1.1–23 mg/m^3 in breathing zone samples (mean, 3.6 mg/m^3). Other potential exposures in sulfuric acid plants include iron disulfide (starting material for sulfur dioxide), ferric oxide (end-product of roasting of iron disulfide), sulfur trioxide (intermediate), vanadium pentoxide (catalyst) and sulfuric acid (end-product). If iron disulfide includes arsenic as an impurity, small amounts of arsenic oxides may also be present in the air of the roasting departments of the plants. Concentrations of total dust, arsenic and quartz were reported (Englander *et al.*, 1988).

In a Finnish sulfuric acid plant, the concentration of sulfuric acid in seven air samples ranged from none detected to 1.7 mg/m^3, with a mean concentration of 0.9 mg/m^3 (Skyttä, 1978). Air concentrations of sulfuric acid in three area samples taken in a sulfuric acid plant at a US copper smelter in 1984 were 0.15–0.24 mg/m^3 (mean, 0.21 mg/m^3) (Gunter & Seligman, 1984). The concentration of sulfuric acid in working area samples in a Russian sulfuric acid plant ranged from 1.8 to 4.6 mg/m^3 (Petrov, 1987); that in general area samples was 0.5–2.4 mg/m^3.

1.4.5 *Soap and detergent manufacture*

Sulfuric acid concentrations measured in 1974 in the air in a soap production plant in Italy were 0.64–1.12 mg/m^3 in the hydrolysis and saponification areas. Other exposures were to soap powder, glycerol, fatty acids, nickel and its compounds (up to 0.07 mg/m^3) and mineral oils (see IARC, 1987) (1.2 mg/m^3) (Forastiere *et al.*, 1987).

1.4.6 *Nitric acid manufacture*

Most nitric acid is manufactured by the catalytic oxidation of ammonia in air in the presence of a platinum catalyst. No data on occupational exposures have been published.

1.4.7 *Phosphate fertilizer manufacture*

Table 10 summarizes occupational exposures to acid mists and vapours in the phosphate fertilizer manufacturing industry. Workers in the phosphate fertilizer industry are potentially exposed to calcium phosphate minerals (including calcium fluoride), sulfuric acid, phosphoric acid (partly as phosphorus pentoxide), calcium sulfate, ammonia and ammonium phosphate (see section 1.2.7). Other potential exposures during mining and chemical processing of phosphate rocks include silica, chromium, arsenic, vanadium and alpha and gamma radiation from uranium-238 and radium-226 impurities of phosphate minerals. In two studies, exposure to ionizing radiation was reported to be low in comparison with recommended standards (Herrick, 1982; Checkoway *et al.*, 1985a).

1.4.8 *Lead battery (accumulator) manufacture*

Sulfuric acid is used in the manufacture of lead–acid batteries. The highest exposures have been found in plate forming, where lead plates are immersed in tanks of dilute sulfuric acid through which a current is passed. Gas bubbles generate an acid mist above the tanks. In the forming process, the lead plates are fused and then encased in a shell to prepare them for charging; or the battery is filled with acid and charged with direct current. Table 11 presents the available data on occupational exposures to sulfuric acid in this industry, the highest value found being 11.6 mg/m^3.

In a study of five battery manufacturing plants in the USA, the highest levels of sulfuric acid mist were usually measured in forming, and sometimes in charging, assembly and battery repair. The concentrations of lead, arsine and stibine in air during forming also tend to be higher than in most other operations (Jones & Gamble, 1984).

Only one study was available to the Working Group on the particle size distribution of acid mists in the work environment. In a study of five US battery manufacturing plants, the average mass median aerodynamic diameter of H_2SO_4 mist was 5–6 μm, with an average geometric standard deviation of 4–5 μm, depending on the impactor used (Jones & Gamble, 1984).

1.4.9 *Other industries*

Table 12 summarizes the available data on occupational exposures in other industries in which acid mists or vapours may be generated. Although the numbers of measurements were often limited, the highest exposures were to hydrochloric acid during titanium dioxide production in the USSR (Feigin, 1986), in the sand chlorination area of a zirconium and hafnium plant in the USA (Apol & Tanaka, 1978), during short-term exposure of fire fighters during a training exercise in the USA (Zey & Richardson, 1989) and during painting in Finland (FIOH, 1990) and to phosphoric acid during fertilizer production in Finland (FIOH, 1990).

1.5 Regulations and guidelines

Occupational exposure limits for sulfuric acid in some countries or regions are presented in Table 13; those for nitric acid and for phosphoric acid are presented in Tables 14 and 15, respectively. Those for hydrochloric acid are given in the monograph on p. 196.

Table 10. Occupational exposures to strong inorganic acid mists and vapours during phosphate fertilizer manufacture

Operation/process	Acid	Sample	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
				Mean	Range			
Acid tanks, compressors, precipitation	HNO_3	NR	5	38.7	1.8–14.5	1965	Finland	FIOH (1990)
Process operator	HNO_3	NR	1	1.3				
Cleaning phosphoric acid reactor vessel in phosphate fertilizer/-phosphoric acid production	H_2SO_4	Area	8	< 0.07		1975	USA	Cassady *et al.* (1975)
	H_3PO_4	Area	9	0.25	< 0.005–2.12			
Cleaning H_3PO_4 reactor vessel	H_3PO_4	NR	NR	NR	0.02–0.08	1975	USA	Wolf & Cassady (1976)
	H_2SO_4	NR	NR	NR	0.08–0.13			
Cleaning H_3PO_4 reactor vessel	H_3PO_4	Personal	9	0.075	0.03–0.129	1976	USA	Stephenson *et al.* (1977a)
	H_2SO_4	Personal	11	0.571	0.16–3.31			
Cleaning H_3PO_4 reactor vessel	H_3PO_4	Personal	4	0.183	0.03–0.25	1976	USA	Stephenson *et al.* (1977b)
	H_2SO_4	Personal	3	0.068	0.013–0.16			
General area	H_3PO_4	Area	4	0.31	0.17–0.52			
	H_2SO_4	Area	5	0.136	0.03–0.22			
Phosphoric acid evaporation and agitation in ammonium phosphate fertilizer production	H_3PO_4	Personal	11	0.34	< 0.05–3.43	1985	USA	Apol & Singal (1987)
	H_2SO_4	Personal	11	0.13	< 0.05–1.26			
Drilling level in superphosphate fertilizer manufacture	H_2SO_4	NR	1	0.3		1957	Finland	FIOH (1990)
	H_2SO_4^{a}	NR	1	8.3		1951		
Superphosphate plant, work area	H_2SO_4	NR	NR	NR	5.2–9.2	NR	USSR	Tadzhibaeva & Gol'eva (1976)
	H_2SO_4	NR	NR	NR	2.7–4.4			

NR, not reported

[a] Concentration of sulfur trioxide calculated as sulfuric acid

Table 11. Occupational exposures to sulfuric acid mists during lead battery (accumulator) manufacture

Operation/process	Sample	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
			Mean	Range			
Accumulator room in electricity plant, worst case		1	11.6		1955	Finland	FIOH (1990)
Plate forming		NR	> 16 (humid day)	3.0–16.6 (dry day)	NR	USA	Malcolm & Paul (1961)
Charging		NR		< 0.8–2.5			
Plate forming	Area Area	38 12	1.38 0.971	< 0.183– > 5.618 < 0.221–3.517	NR	Wales (UK)	Anfield & Warner (1968)
Battery manufacture	Area	> 12 > 12		26.1–35.0 12.6–13.5	NR	Egypt	El-Sadik *et al.* (1972)
Forming		3	0.16	0.07–0.25	1971, 1973, 1975	Finland	Skyttä (1978)
Charging in brewery battery shop		33	< 0.1		1976	USA	Rivera (1976)
Acid room	Area	1	0.03		1978	USA	Young (1979c)
Charging	Area	1	0.04				
Assembly	Area	1	0.03				
Charging	Area	1	0.107		1978	USA	Young (1979d)
Wetdown area	Area	1	0.064				
Acid room	Area	1	0.141				
Forming	NR	1	1.03		1978	USA	Young (1979e)
Acid room	NR	1	0.09				
Charging	NR	1	0.03				
Various	Personal Personal Personal Personal Personal Personal	2 4 14 15 9 3		0.1– > 0.1 0.08–0.1 0.06–0.08 0.04–0.06 0.02–0.04 < 0.02	1979	USA	Costello & Landrigan (1980)

Table 11 (contd)

Operation/process	Sample	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
			Mean	Range			
Charging in municipal transit battery shop	Personal Area	1 1	0.029 0.068		1980	USA	Hartle (1980)
Charging in diesel engine and locomotive manufacture	Personal Area	12 12	0.015 0.024	0.01–0.027 0.008–0.040	1980	USA	Lucas & Cone (1982)
Various Forming	Personal Area	9 1	< 0.18 < 0.19		1984	USA	Singal *et al.* (1985)
Various	Personal	18 55 37 57 58	0.08 0.14 0.08 0.35 0.16	SD, 0.07 SD, 0.14 SD, 0.08 SD, 0.35 SD, 0.21	NR	USA	Jones & Gamble (1984)
Lead-acid battery recharge	Area	4	0.01	0.009–0.011	1988	USA	Daniels (1988)
Short term	Personal	4	0.09	0.05–0.12			
Full shift	Personal	1	0.015				

NR, not reported

Table 12. Occupational exposures to strong inorganic acid mists and vapours in various industries

Acid	Operation	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
				Mean	Range			
H_2SO_4	Acid preparation in paper mill	NR	3	4.5	0.3–11.5	1951	Finland	FIOH (1990)
	Paper machine	NR	4	6.3	2.7–8.9	1951–59		
	Hall near acid tanks and storage	NR	3	0.6	0.5–0.8	1959		
	Copper smelter[a]	NR	17	1.0	< 0.1–3.7	1952–57		
	Nitrocellulose manufacture: oleum storage, denitration, acid centrifuge, mixing of acid	NR	4	0.7	0.2–1.2	1952		
	Sulfite pulp production: acid plant[a]	NR	3	< 0.2		1954–55		
	leakage	NR	1	18				
	Reaction, filtering, evaporation in titanium dioxide manufacture	NR	5	0.4	0.3–0.8	1961		
	Reaction	NR	1	2.3		1971–74		Skyttä (1978)
	Dissolving	NR	1	1.0				
	Filtering, control	NR	2	0.4	0.2–0.5			
	Waste treatment plant in aircraft maintenance facility	NR	2	< 0.015		1972	USA	Hervin & Reifschneider (1973)
	Heating, slag removal, water treatment at power plant	NR	1	0.6		1972	Finland	Skyttä (1978)
	Electrolytic treatment in offset printing	NR	3	0.2	ND–0.5	1974–76		
	Extraction in ammonium phosphate production	NR	NR	NR	2.5–14	NR	USSR	Danielyants (1976)
	Tollbooth in national park	Personal and area	11	0.52	0.18–1.14	1976	USA	Haas & Geissert (1976)
	Guard booth at border crossing	NR	4	ND		1979	USA	Markel & Ruhe (1981)
	Desulfurization control room in coke plant	Area	1	0.014		1979	USA	Lewis (1980)
	Volcano observation	NR	1	1.0		1979	USA	Belanger (1980)
	Cement company	Area	10	0.05	ND–0.2	1980	USA	Jankovic (1980)
		Personal	4	0.15	0.1–0.22			

Table 12 (contd)

Acid	Operation	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
				Mean	Range			
H_2SO_4 (contd)	Paper machine tending	Personal and area	27	0.01	< 0.01–0.06	1981	USA	Apol (1981b)
	Alum batch processing	Personal Area	3 4	0.5 0.08	0.09–0.38 0.03–0.2	1981	USA	McGlothlin *et al.* (1982)
	Deliming and bating in chrome leather tannery	NR	6	0.48	0–0.96	1981	USA	Stern *et al.* (1987)
	Belly pickling in leather manufacture	Personal	2	0.18	0.16–0.20	1982	USA	Fajen (1982)
	Tanning	Area	3	0.16	0.12–0.20			
	Wet milling in corn starch production	Area	NR	NR	< 0.04–0.05	1985	USA	Almaguer & London (1986)
	Photography lab	Personal Area	1 1	0.02 < 0.003		1985	USA	Hunninen (1986)
	Pigmentary titanium dioxide production area	Area	NR	NR	2.03–3.66	NR	USSR	Feigin (1986)
	Mixing of odourizing chemicals	Area Personal	4 2	< 0.02 < 0.02		1987	USA	Pryor (1987)
	Wet milling of corn products	Area	3	1.7	0.7–2.5	1988	USA	Gunter (1988)
HCl	Agricultural research	NR	2	11.8	8.5–15	1951	Finland	FIOH (1990)
	Cooling department in HCl plant	NR	1	4		1954		
	Reaction department in TiO_2 plant	NR	4	2	0.08–0.5	1961		
	Furnaces, HCl absorption plant, charging in $NaSO_2$ plant	NR	28	6.4	1.3–23.8	1963–67		
	Reactor, evaporators, driers in $CaCl_2$ plant	NR	13	1.3	ND–6.9	1963–67		
	Etching of offset printing plates	NR	1	15		1966		
	Pressing of records	NR	4	ND		1966		
	Acid room in electric bulb plant	NR	1	3.1		1966		
	Tin soldering with HCl	NR	4	8.2	6.0–10.4	1967–68		
	Welding in metalware plant	NR	2	ND		1967–68		
	Etching of offset printing plates	NR	9	3.7	0.15–18	1971–76		Skyttä (1978)
	Drying of offset printing plates	NR	1	3.9		1974		
	Burning resin in offset printing plant	NR	1	0.45		1976		

Table 12 (contd)

Acid	Operation	Sample type	No. of samples	Air concentration (mg/m^3)		Year of measurement	Country	Reference
				Mean	Range			
HCl (contd)	Chemical storage	NR	1	60		1972	Finland	Skyttä (1978)
	Mixing of lime, drying of sewage sludge	NR	2	0.75				
	Sand chlorination in zirconium and hafnium extraction	Area	9	3.6	0.08–7.3	1975–77	USA	Apol & Tanaka (1978)
	Heating, slag removal, water treatment in power plant	NR	2	0.6	0.5–0.7	1976	Finland	Skyttä (1978)
	Zinc die casting in automobile parts plant	Area	2	0.05	ND–0.1	1977	USA	Gilles *et al.* (1977)
	Superwash treatment, seaming	NR	2	2.16	0.75–3.58	1975, 1976	Finland	Skyttä (1978)
	Organic flocculant batch mixing	Area Personal	3 1	0.08 ND	ND–0.14	1981	USA	McGlothlin *et al.* (1982)
	Extrusion in polyvinyl chloride container plant	Area Area Personal	3 6 2	0.25 < 0.005 < 0.005	0.19–0.28	1982	USA	Lucas & Schloemer (1982)
	Wet milling in corn starch plant	Area	NR	NR	< 0.02–0.93	NR	USA	Almaguer & London (1986)
	Working area in TiO_2 production	NR	NR	9.67	4.46–13.39	NR	USSR	Feigin (1986)
	Smoke bomb during firefighting training	NR	8	18.2	1.9–44	1987	USA	Zey & Richardson (1989)
	Wet milling in corn products plant	Area	3	0.04	0.03–0.06	1988	USA	Gunter (1988)
HNO_3	Pumps, presses in lanthanide plant	NR	2	1.6	1.0–1.8	1965	Finland	FIOH (1990)
	Printing machines (relief)	NR	1	1.03		1971	Finland	Skyttä (1978)
	Cleaning relief printing plates	NR	1	1.3		1971		
	Print-making in art college	Personal Area	2 1	0.83 0.06	0.50–1.15	1976	USA	Levy (1976)
	Wet milling in corn products plant	Area	3	ND		1988	USA	Gunter (1988)
H_3PO_4	Phosphoric acid production	NR	NR	0.31	0.07–0.62	1974	Italy	Fabbri *et al.* (1977)
	Wet milling in corn products plant	Area	3	0.40	0.23–0.68	1988	USA	Gunter (1988)

NR, not reported; ND, not detected or below detection limit

[a] Concentration of sulfur trioxide calculated as sulfuric acid

Table 13. Occupational exposure limits and guidelines for sulfuric acid

Country or region	Year	Concentration (mg/m^3)	Interpretation[a]
Australia	1990	1	TWA
Austria	1982	1	TWA
Belgium	1990	1	TWA
		3	STEL
Bulgaria	1984	1	TWA
Chile	1983	0.8	TWA
China	1979	2	TWA
Czechoslovakia	1990	1	TWA
		2	STEL
Denmark	1990	1	TWA
Finland	1990	1[b]	TWA
		3[b]	STEL (15 min)
France	1990	1	TWA
		3	STEL
Germany	1990	1[b]	TWA
Hungary	1990	1	STEL
India	1983	1	TWA
Indonesia	1978	1	TWA
Italy	1978	1	TWA
Japan	1990	1	TWA
Mexico	1983	1	TWA
Netherlands	1985	1	TWA
Norway	1990	1	TWA
Poland	1990	1	TWA
Romania	1975	0.5	TWA
		1.5	Ceiling
Sweden	1990	1	TWA
		3	STEL (15 min)
Switzerland	1990	1	TWA
		2	STEL
Taiwan	1981	1	TWA
United Kingdom	1990	1	TWA
USA			
ACGIH	1990	1	TWA
		3	STEL
OSHA	1989	1	TWA
USSR	1990	1[b]	STEL

Table 13 (contd)

Country or region	Year	Concentration (mg/m^3)	Interpretation[a]
Venezuela	1978	1	TWA
		1	Ceiling
Yugoslavia	1971	1	TWA

From Cook (1987); US Occupational Safety and Health Administration (OSHA) (1989); American Conference of Governmental Industrial Hygienists (ACGIH) (1990); Direktoratet for Arbeidstilsynet (1990); International Labour Office (1991)

[a] TWA, full-shift time-weighted average; STEL, short-term exposure limit

[b] Skin irritant notation

Table 14. Occupational exposure limits and guidelines for nitric acid (CAS No. 7697-37-2)

Country or region	Year	Concentration (mg/m^3)	Interpretation[a]
Australia	1990	5	TWA
		10	STEL
Austria	1990	5.2	TWA
		10	STEL
Belgium	1990	5.2	TWA
		10	STEL
Chile	1983	4	TWA
Czechoslovakia	1990	2.5	TWA
		5	STEL
Denmark	1990	5	TWA
Germany	1990	25[b]	TWA
Finland	1990	5	TWA
		13	STEL (15 min)
France	1990	5	TWA
		10	STEL
Hungary	1990	5	STEL
India	1983	5	TWA
		10	STEL
Indonesia	1978	5	TWA
Italy	1978	5	TWA
Japan	1990	5.2	TWA
Mexico	1983	5	TWA
Netherlands	1986	5	TWA
Norway	1990	5	TWA
Poland	1990	10	TWA
Romania	1975	4	TWA
		10	Ceiling
Sweden	1990	5	TWA
		13	STEL (15 min)

Table 14 (contd)

Country or region	Year	Concentration (mg/m^3)	Interpretation[a]
Switzerland	1990	5	TWA
		10	STEL
Taiwan	1981	25	TWA
United Kingdom	1990	5	TWA
		10	STEL (10 min)
USA			
ACGIH	1990	5.2	TWA
		10	STEL
OSHA	1989	5	TWA
Venezuela	1978	5	TWA
		10	Ceiling
Yugoslavia	1971	25	TWA
USSR	1990	2	STEL

From Cook (1987); US Occupational Safety and Health Administration (OSHA) (1989); American Conference of Governmental Industrial Hygienists (ACGIH) (1990); Direktoratet for Arbeidstilsynet (1990); International Labour Office (1991)

[a] TWA, full-shift time-weighted average; STEL, short-term exposure limit

[b] Skin irritant notation

Table 15. Occupational exposure limits and guidelines for phosphoric acid (CAS No. 7664-38-2)

Country or region	Year	Concentration (mg/m^3)	Interpretation[a]
Australia	1990	1	TWA
		3	STEL
Belgium	1990	1	TWA
		3	STEL
Denmark	1990	1	TWA
Finland	1990	1[b]	TWA
		3[b]	STEL (15-min)
France	1990	1	TWA
		3	STEL
Indonesia	1978	1	TWA
Italy	1978	1	TWA
Japan	1990	1	TWA
Netherlands	1986	1	TWA
Norway	1990	1	TWA
Sweden	1990	1	TWA
		3	STEL (15-min)
Switzerland	1990	1	TWA

Table 15 (contd)

Country or region	Year	Concentration (mg/m^3)	Interpretation[a]
United Kingdom	1990	1	TWA
		3	STEL (10-min)
USA			
ACGIH	1990	1	TWA
		3	STEL
Venezuela	1978	1	TWA
		3	Ceiling
Yugoslavia	1971	1	TWA

From Cook (1987); American Conference of Governmental Industrial Hygienists (ACGIH) (1990); Direktoratet for Arbeidstilsynet (1990); International Labour Office (1991)

[a]TWA, full-shift time-weighted average; STEL, short-term exposure limit
[b]Skin irritant notation

2. Studies of Cancer in Humans

2.1 Case reports

Fifteen of the 30 cases of primary bronchial cancer seen in a hospital ward in Frankfurt, Germany, were from a plant which produced, up to 1931, sulfuric acid, hydrochloric acid and sulfates, secondary to the production of chromate (Alwens *et al.*, 1936). Four cases occurred among workers exposed only to acids for 24, 28, 31 and 42 years. Six of the 15 workers had worked exclusively in the chromate workshop, with employment periods ranging from 22 to 40 years.

2.2 Cohort studies

The cohort studies described below are summarized in Table 16 (p. 90).

2.2.1 *Isopropanol manufacture*

A cohort study of US chemical workers (Weil *et al.*, 1952) based on death claims for employees active in 1928–50 revealed 258 deaths from all causes; 34 (13.2%) were deaths due to cancer. This did not represent an excess when compared to US proportional mortality rates. A total of 182 workers had been employed in the isopropanol unit of the South Charleston plant studied by Teta *et al.*, 1992 (see p. 82) between 1928 and 1950; 71 had worked for more than five years, and 37 had worked for more than 10 years. Four of the six respiratory tract cancers observed were in the sinuses (in two workers who died and in two who survived), one was of the lung (in one dead worker) and one was of the larynx (in one surviving worker). The three who died were aged 30 to early 40s, but the age at diagnosis of the remaining three cases was not given. All six workers with cancer had worked for more than five years in the unit, and their exposure had started in the early 1930s, before any change was made in the unit. A highly significant excess risk for cancer of the paranasal sinuses was seen on comparison with the expected number, based on the US rate of 0.2%. [The Working Group noted that it was not clear what methods were used to enumerate the cohort; however, the excess was so large as to render this concern inconsequential.]

Hueper (1966) reviewed the data described by Weil *et al.* (1952) and a report by Eckardt (1959) of three cases of sinus cancer and two of cancer of the intrinsic larynx among workers at another isopropanol manufacturing plant. Hueper calculated a highly significant, age-specific excess incidence in men aged 45–54 years with at least nine years in isopropanol production; the relative risk is 21 for cancers of the nasal sinuses and larynx combined based on four cases [95% confidence interval (CI), 5.7–53.9]. [The Working Group noted that the basis for the comparison is not clear.]

A cohort study was carried out among 262 men who had been employed for at least one year during 1949–75 at an isopropanol plant in the United Kingdom and followed up to 1975 (Alderson & Rattan, 1980). There were 26 deaths (standardized mortality ratio [SMR], 1.10 [95% CI, 0.72–1.61]), including nine from cancer (SMR, 1.45 [95% CI, 0.67–2.76]). One man died from nasal cancer (0.02 expected), and two each from lung cancer (SMR, 0.78 [95% CI, 0.09–2.8]), kidney cancer (SMR, 6.45 [95% CI, 0.8–23.3]) and brain tumour (SMR, 16.67 [95% CI, 2.0–60.2]).

Enterline (1982) briefly reported results for 54 deaths among 433 workers employed for more than three months in an isopropanol unit in Texas (USA) between 1941 and 1965, with follow-up through 1978. Compared to rates in Texas, mortality from all causes was significantly low (54 deaths; SMR, 0.65 [95% CI, 0.49–0.84]), while the SMR for cancers at all sites was 0.99 (16 deaths [95% CI, 0.57–1.61]); there were two deaths from cancer of the buccal cavity and pharynx (0.50 expected) and seven deaths from lung cancer (SMR, 1.18 [95% CI, 0.47–2.43]). Four of the seven subjects who died from lung cancer had also worked in an epichlorohydrin unit (SMR, 2.48 [95% CI, 0.67–6.36]); the other three had a low risk of lung cancer (SMR, 0.69 [95% CI, 0.14–2.02]). Neither of the subjects with cancer of the buccal cavity and pharynx had worked with epichlorohydrin, and their high risk was attributed to employment in the isopropanol unit.

2.2.2 *Manufacture of synthetic ethanol and isopropanol by the strong acid process*

A historical cohort study was conducted of 335 process workers (Lynch *et al.*, 1979) who had had one month or more employment in an isopropanol plant and an ethanol plant in a petrochemical complex in Baton Rouge, LA (USA), between 1950 and 1976. A total of 255 were still alive, 48 dead and 32 lost to follow-up; two women were excluded from the analyses. Comparison rates were based on US white male rates from the Third National Cancer Survey for 1969–71. The standardized incidence ratio (SIR) for laryngeal cancer in this cohort was 5.04 [95% CI, 1.36–12.90], based on four cases. In an expanded cohort of 740 men, including both process workers and mechanical craftsmen and supervisors, the SIR was 3.2 [1.3–6.6], based on seven cases. Presumed exposure to diethyl sulfate was tentatively implicated. (See also the study by Soskolne *et al.*, 1984, p. 89.)

The mortality experience of 538 men employed as ethanol and isopropanol process workers in a Union Carbide chemical plant in South Charleston (SC) and 493 at a plant in Texas City (TC), all of whom had been employed for one month or more from 1941 through 1978, was followed from the early 1940s to 1983 (Teta *et al.*, 1992). The SC plant produced ethanol from 1930 to 1968 and isopropanol from 1928 to 1949, using strong sulfuric acid in each process. The TC plant used strong sulfuric acid in the production of ethanol from 1941 to 1968 but switched in 1969 to a process employing the hydration of ethylene; this plant also used strong sulfuric acid for the production of isopropanol from 1941 to 1949, when they changed to a weak-acid process. External comparisons were made to national US and regional rates. For the two plants combined, there were 300 deaths (29% of the cohort), and nine subjects were lost to follow-up. All subjects who died in the SC plant had had an exposure assignment to the strong sulfuric acid units. Mortality from all causes and from malignant neoplasms at all sites for the combined cohort of strong-acid workers in the two plants was approximately as expected. The mortality rate for lung cancer was not elevated (22 deaths [SMR, 0.94; 95% CI, 0.59–1.43]); there were two deaths from laryngeal cancer [SMR, 2.00; 95% CI, 0.22–7.22] and three from cancer of the buccal cavity and pharynx [SMR, 1.36; 95% CI, 0.27–3.98]). A significant excess of deaths from lymphoma and reticulosarcoma was restricted to workers at the SC plant who had had fewer than five years of employment. One sinus cancer was reported among workers at the SC plant prior to 1950, but no reference rates were available. No cancer death was seen among weak-acid workers (1.9 expected). The one death due to laryngeal cancer and the two deaths due to cancer of the buccal cavity and pharynx in the SC plant (strong-acid process) were seen in men with fewer than five years of employment in the plant.

2.2.3 *Pickling and other acid treatment of metals*

Mazumdar *et al.* (1975) reported on a cohort study of mortality among white sheet and tin mill workers, including pickling workers, in an updating of their longitudinal study of Allegheny County (USA) steelworkers, 1953–66. Men involved in batch pickling and sheet drying (n = 55), coating (n = 328), continuous pickling and electric cleaning (n = 205), sheet finishing and shipping (n = 1733), stainless annealing, pickling and processing (n = 46) and tin finishing and shipping (n = 396) were included. Cancer of the respiratory organs occurred in 27 of 2763 men employed in these areas [SMR, 1.10; 95% CI, 0.73–1.60]. [The Working Group combined results for the work areas where there was assumed to be opportunity for exposure to acid aerosols and mists.]

Ahlborg *et al.* (1981) reported three incident cases of 'medium, differentiated' squamous laryngeal cancers diagnosed between 1971 and 1978 among 110 men employed for at least one year between 1951 and 1979 in a small Swedish factory unit for the pickling and processing of stainless-steel pipes, whereas 0.06 were expected on the basis of reference rates from the Swedish Cancer Registry. All three men had smoked 10–15 cigarettes per day for many years. All three had first been employed $\geq$ 10 years before the cancer was diagnosed. Exposure during the 1950s was to pickling baths containing sulfuric and nitric acids and that during the 1960s and 1970s to oxalic acid, ammonium bifluoride and soap. There was also one case of bronchial carcinoma.

In a cohort study undertaken by the US National Institute for Occupational Safety and Health (NIOSH) (Beaumont *et al.*, 1987), the mortality patterns of 1165 male workers employed from 1940 to 1964 and exposed to sulfuric and other acid mists (primarily hydrochloric acid mist) in three steel-pickling operations for at least six months were examined through October 1981. Of the full cohort, 722 had been exposed only to sulfuric acid (595 probably had daily exposure) and 254 to sulfuric acid and other acid mists; 189 had been exposed to acids other than sulfuric. The exposure of all workers averaged 8.8 years (Steenland & Beaumont, 1989). Pickling workers who had ever been employed in coke ovens were excluded. In a health hazard evaluation conducted by NIOSH in 1977 in the largest facility, exposures to a number of agents were measured, including iron oxide, lead, nickel, chromium and respirable silica; detectable levels were found only of iron oxide and lead. There were 326 deaths in the cohort; death certificates were not obtained for 22, and vital status was not ascertained for 15 (1.3%) individuals. Mortality from causes of death other than lung cancer was unremarkable. Analysis of the full cohort for exposure to any acid, using US death rates as the standard, showed mortality from lung cancer to be significantly elevated (SMR, 1.64; 95% CI, 1.14–2.28), based on 35 observed deaths. The SMR was 1.85 (95% CI, 1.25–2.64) for men with more than 20 years since first exposure to any acid, but was not related to duration of exposure. For those with probable daily exposure to sulfuric acid, all of the excess risk occurred 20 years or more after first employment (SMR, 1.93; 95% CI, 1.10–3.13). For men exposed to sulfuric acid only, the SMR for lung cancer was 1.39 ([95% CI, 0.84–2.17], 19 deaths); for those with probable daily exposure to sulfuric acid only, it was 1.58 ([95% CI, 0.94–2.50], 18 deaths); for those exposed to sulfuric and other acids, it was 1.92 ([95% CI, 0.77–3.95], seven deaths); for those exposed to acids other than sulfuric acid, it was 2.24 [95% CI, 1.02–4.25]; 9 deaths). No dose–response relationship was evident for men who had held jobs with probable daily exposure to sulfuric acid, using length of employment as the measure of exposure. Using another steelworker group for comparison and adjusting for the probable distribution of smoking habits, it was shown that smoking was unlikely to explain the increased lung cancer risk entirely.

Steenland and Beaumont (1989) extended the period of follow-up of the cohort of Beaumont *et al.* (1987) from November 1981 through early 1986 and obtained additional information: 73% of the men themselves or their next-of-kin were contacted to determine vital status and smoking habits. Indirect adjustment was made for smoking using the technique of Axelson (1978), taking into account observed differences in smoking habits between the cohort and the US referent population. The SMR for lung cancer was 1.55 (95% CI, 1.12–2.11), based on 41 deaths and unadjusted for smoking; the adjusted SMR was 1.36 (95% CI, 0.97–1.84). For men with 20 or more years since first exposure, the unadjusted SMR was 1.72 (95% CI, 1.21–2.39); that adjusted for smoking was 1.50 (95% CI, 1.05–2.27). Using duration as a measure of exposure did not result in a dose–response trend, although the authors state that duration may be a poor surrogate of exposure.

Steenland *et al.* (1988) conducted an interview-based study of laryngeal cancer incidence, using a subset (77%) of the population studied by Beaumont *et al.* (1987) comprising all men for whom adequate information could be obtained to determine the incidence of laryngeal cancer. Follow-up through 1985 rendered 47 additional deaths, for a total of 373 deaths, or 32% of the entire cohort. The smoking habits of 795 and the drinking habits of 593 male steelworkers exposed to acid mists during pickling operations were determined. The average duration of exposure was 9.5 years. Nine laryngeal cancer cases were confirmed. Using data from national surveys of cancer incidence as referent rates, 3.44 laryngeal cancers would have been expected [relative risk, 2.6; 95% CI, 1.2–5.0]. As the exposed cohort smoked more than the US population, the expected number of cases was raised to 3.92, giving an SIR of 2.30 [95% CI, 1.05–4.36].

2.2.4 *Sulfuric acid manufacture*

Seven lung cancer cases were diagnosed during an 11-year period (1957–67) in a group of 259 blue-collar workers at a sulfuric acid plant in Germany (Thiess *et al.*, 1969). The patients had been employed at the plant for periods of six months to 32 years. Six were smokers (the smoking habits of the other case were unknown). The authors calculated an incidence of 268 per 10 000 employees at the sulfuric acid plant and 39.8 per 10 000 among other workers in the factory. A further lung cancer case occurred in an office worker at the same plant, who was a smoker. [The Working Group noted the incomplete reporting of methodology; e.g., the extent of follow-up of the employees.]

Mortality and cancer incidence were evaluated among workers employed at a sulfuric acid plant that has been operating since 1932 in Sweden (Englander *et al*, 1988). Industrial hygiene data, available between 1969 and 1984, indicated possible exposure of the respiratory zone to the following substances: sulfur dioxide (median of yearly time-weighted averages, 3.6 mg/m^3), arsenic (11 µg/m^3), total dust (2.2 mg/m^3), respirable dust (0.6 mg/m^3) and sulfuric acid (occasional measurements; range, $<$ 0.1–2.9 mg/m^3). A total of 400 workers who had been employed for at least six months during the period 1 July 1960 to 31 December 1981 were identified from company records and followed up through 1985; two subjects were lost to follow-up. The vast majority of the workers had been employed for fewer than 25 years. Information about tumours diagnosed between 1961 and 1985 among cohort members and reference rates for cancer incidence in the county were obtained from the Southern Swedish Regional Tumour Register. Mortality from all causes was higher than expected (53 deaths (all with death certificates available); SMR, 1.48 [95% CI, 1.11–1.94]), whereas the number of cancer deaths was about that expected (eight deaths; SMR, 0.88 [95% CI, 0.38–1.73]; 23 cancers diagnosed; SIR, 1.34 [95% CI, 0.85–2.02]). There were excess numbers of respiratory cancers (five cases; SIR, 2.00 [95% CI, 0.50–4.67]) and bladder cancers (five cases; SIR, 3.77 [95% CI, 1.25–8.98]). The risk for bladder cancer was higher among workers with five or more years since first employment (five cases; SIR, 4.36 [95% CI, 1.35–9.72]), but the risk for respiratory cancer was not higher in this subgroup (four cases; SIR, 1.83 [95% CI, 0.50–4.69]).

Sulfuric acid was manufactured at some of the smelters on which studies are reported in the monograph on sulfur dioxide. The predominant exposure at the smelters, however, was to sulfur dioxide, and results on exposure to acid mists were not reported.

2.2.5 *Soap and detergent manufacture*

Workers at a factory in central Italy which produced solid soap were studied for mortality and incidence of laryngeal cancer (Forastiere *et al.*, 1987). According to measurements taken in 1974, workers were exposed to sulfuric acid mists (0.64–1.12 mg/m^3), nickel and its compounds (up to 0.07 mg/m^3) and mineral oils (1.2 mg/m^3); soap powder, glycerol and fatty acids were also present. From company records, 361 men active on 1 January 1964 or hired thereafter until 1972 and employed for at least one year were enrolled. Follow-up for vital status lasted from 1 January 1969 to 30 June 1983 and was completed for 347 (96%) cohort members. Cause of death was obtained for all deceased individuals. Laryngeal cancer incidence was ascertained (from 1 January 1972 to 30 June 1983) by reviewing the discharge files of the ear, nose and throat departments of local hospitals. SMRs were calculated using the mortality figures of the province as reference; expected numbers of laryngeal cancer cases were estimated according to both incidence rates from four European cancer registers and data derived from the local search. Fewer than the expected number of deaths occurred from all causes (30 deaths; SMR, 0.70; 95% CI, 0.47–1.00) as well as from all cancers (eight deaths; SMR, 0.71; 95% CI, 0.31–1.39). One subject died of laryngeal cancer (0.6 expected), and five lung cancer deaths were recorded (SMR, 1.69; 95% CI, 0.55–3.86). Five laryngeal cancer cases were detected (including the death), yielding an SIR of [6.94 (95% CI, 2.25–16.2)] or [3.47 (95% CI, 1.13–8.10)], depending on the reference population chosen. All of the cancers occurred among subjects with more than 10 years since first employment and with 4–27 years' duration of exposure.

2.2.6 *Nitric acid manufacture*

Cancer incidence was investigated among production and maintenance workers at a nitric acid production plant within an electrochemical industrial complex in southern Norway (Hilt *et al.*, 1985). A group of 287 men who had been exposed to asbestos between 1928 and 1980 was divided according to degree of exposure to asbestos. The 190 workers who were only indirectly exposed to asbestos (mechanics, plumbers, welders and production workers) but were also exposed to nitrous gases, nitric acid vapours and ammonia and who had had at least one year of exposure at the plant are considered here. Mortality from all causes in this group in 1953–80 was about as expected (75 deaths; SMR, 1.07 [95% CI, 0.84–1.34]), and the incidence of cancers at all sites in the same period was not increased (19 cases; SIR, 0.95; 95% CI, 0.6–1.5). Five cases of cancer of the lung and one of the pleura were detected, while a total of 2.5 cases was expected (SIR, 2.4; 95% CI, 0.92–5.4); there were also five cancers of unknown origin (SIR, 5.4; 95% CI, 1.8–13.0). These excesses were present mainly in maintenance workers, both with regard to respiratory cancer (three cases; SIR, 5.0; 95% CI, 1.03–14.61) and to cancers of unknown origin (four cases; SIR, 21.0; 95% CI, 5.5–51.2); in production workers, three lung cancers and one cancer of unknown origin were observed, while the expected numbers were 1.9 and 0.7, respectively. [The Working Group noted that the possiblity of concomitant exposure to asbestos limits the interpretability of this study with respect to exposure to nitric acid.]

2.2.7 *Phosphate fertilizer manufacture*

Mining and chemical processing of phosphate rocks to obtain phosphate fertilizer involves exposures to several toxic substances (see also section 1.2.7), including ionizing radiation from decay products of uranium (Checkoway *et al.*, 1985a). Concern about possible adverse health effects, especially lung cancer, of exposure to low levels of ionizing radiation during work in phosphate mining and phosphate fertilizer production motivated three independent historical cohort studies among workers in the Florida (USA) phosphate industry (Checkoway *et al.*, 1985a; Stayner *et al.*, 1985; Block *et al.*, 1988).

Men employed for a minimum of three months' continuous service with one of 16 member companies of the Florida Phosphate Council during the years 1949–78 and with at least 12 months' cumulative service were enrolled in a cohort (Checkoway *et al.*, 1985a). Vital status was ascertained for 17 601 white and 4722 non-white men from 1 January 1949 to 31 January 1978: 1620 white and 650 non-white men had died (no death certificate for 56 and 20, respectively); 191 white and 81 non-white subjects were lost to follow up. Race-specific SMRs were calculated, taking both the US and Florida (the latter only for cancer) male populations as comparisons. Among white men, the SMR for all causes was 1.00 and that for overall cancer was 0.95 (289 deaths [95% CI, 0.84–1.07]). Fewer deaths from laryngeal cancer were seen than expected both on the basis of US (three deaths; SMR, 0.66 [95% CI, 0.14–1.93]) and Florida (SMR, 0.59 [95% CI, 0.12–1.72]) standards. Lung cancer mortality was higher than expected on the basis of rates for the US population (117 deaths; SMR, 1.22 [95% CI, 1.01–1.46]); the excess, however, was non-significant when Florida rates were used for comparison (SMR, 1.03 [95% CI, 0.85–1.23]). No clear trend in lung cancer mortality was evident from an analysis of duration of employment, but consistently elevated SMRs were found for men with 30–39 years since first employment (21 deaths; SMR (USA), 1.71; SMR (Florida), 1.52) and for men with 40 or more years since first employment (10 deaths; SMR (USA), 2.08; SMR (Florida), 2.04). Among non-white subjects, the SMR for overall deaths was low (0.80 [95% CI, 0.74–0.86]), whereas it was close to 1.0 for all malignant neoplasms (131 deaths; SMR, 1.02 [95% CI, 0.85–1.21]). Again, lung cancer mortality was increased on the basis of US standards (46 deaths; SMR, 1.24; [95% CI, 0.91–1.65]); this effect was not seen when Florida rates were taken as the comparison (SMR, 1.02 [95% CI, 0.75–1.36]). There was no consistent trend in the SMR for lung cancer with length of employment or with latency since first employment among non-whites. [The Working Group noted that no information was given on the smoking habits of cohort members, which would have been important in view of the possible interaction between smoking and radiation.]

The same data were used for an internal comparison of rates of mortality from lung cancer within the Florida phosphate industry (Checkoway *et al.*, 1985b). Job histories were obtained from the companies, and workers were classified into 16 work areas (one of which included sulfuric and phosphoric acid manufacture) and into several kinds of potential exposure (including phosphoric acid and soluble phosphate, sulfuric acid, sulfur oxides, hydrofluoric acid and soluble fluorides). The analysis was conducted by computing standardized rate ratios (SRRs), adjusted for age and calendar period, within each exposure group across three strata of employment duration (less than one year, the referent category; 1–9 years; 10 years or more). Only subjects employed in skilled crafts and in plant-wide services had a trend for increased risk of lung cancer with duration of employment. No consistent increase in relative risk for lung cancer was found for workers in sulfuric and phosphoric acid production (1–9 years: eight deaths; SRR, 1.34 [95% CI, 0.58–2.64]; > 10 years: three deaths; SRR, 0.87 [95% CI, 0.81–2.54]) or among subjects with potential exposure to acids. Subjects exposed to α radiation or mineral (rock) dust had an excess relative risk, but this did not increase consistently with duration of exposure. [The Working Group noted that the job and exposure categories overlapped.]

A report of three lung cancer cases among workers involved in the cleaning of a phosphoric acid reaction vessel at a phosphate fertilizer production facility in Polk County, Florida, prompted an investigation by researchers at NIOSH (Stayner *et al.*, 1985). In an industrial hygiene survey of the plant, personal and air samples were collected; fluorides (average, 3.39 mg/m^3), sulfuric acid (average, 0.11 mg/m^3) and phosphoric acid (0.25 mg/m^3) were the main contaminants. A total of 3199 subjects, including 212 women, who had worked at the plant from 1953–76 were enrolled and followed-up through December 1977; 113 subjects (3.5%) were lost to follow-up. There were 176 deaths, but death certificates were available for only 163 individuals (calculations were done using only 155 cases). US sex-, age-, time- and race-specific death rates were used to calculate expected number of deaths. Both overall mortality (155 deaths; SMR, 0.82 [95% CI, 0.69–0.96]) and mortality from all cancers (22 deaths; SMR, 0.76 [95% CI, 0.48–1.15]) were lower than expected. The risk for lung cancers among all study subjects was increased only slightly (10 deaths; SMR, 1.13 [95% CI, 0.54–2.08]), but five deaths occurred among black subjects, to yield an SMR of 1.82 [95% CI, 0.59–4.26]. Among black men with ≥ 20 years of duration of exposure and latency, two cases of lung cancer were seen, whereas 0.16 were expected. The initial three cases of lung cancer, which also occurred among black men, gave an SMR of [1.27; 95% CI, 0.26–3.71].

Male workers employed for six months or more between 1950 and 1979 at a Florida phosphate company were included in a cohort followed up through 1981 (Block *et al.*, 1988). Individuals were categorized according to the job area in which they had worked the longest. Workers in chemical/fertilizer had potential exposure to chemical fumes (sulfuric acid, sulfur dioxide and fluorides), silica dust and radiation from radon decay products. Of the 3451 subjects in the study, 486 (for 18 of whom there was no information about cause of death) were found to be deceased, while vital status was unknown for 226 (6.5%). The expected number of deaths was calculated on the basis of race-, age- and time-specific US rates; Florida rates were also considered. A questionnaire including questions on smoking habits was sent to 2155 subjects with one year or more of employment; 992 (46%) replied. Information on cancer occurrence was confirmed from medical records, and SIRs were computed using incidence rates for Connecticut. Mortality from all causes of death was similar to that expected among whites (346 deaths; SMR, 1.00) but was significantly lower among blacks (127 deaths; SMR, 0.74 [95% CI, 0.62–0.88]). Overall cancer rates were increased among whites (86 deaths; SMR, 1.26 [95% CI, 1.01–1.56]) but not among blacks (26 deaths; SMR, 0.93 [95% CI, 0.61–1.36]). Two deaths from laryngeal cancer were reported among whites (SMR, 1.91 [95% CI, 0.23–6.90]) but none among blacks. There was a significant excess of lung cancer deaths (37) among white workers, in comparison to both US rates (SMR, 1.62 [95% CI, 1.14–2.23]) and Florida rates (SMR, 1.50 [95% CI, 1.06–2.07]); no excess of lung cancer was observed among blacks (nine deaths; SMR, 1.04 [95% CI, 0.48–1.97]). Among workers with one year or more of employment, there was an increasing trend in numbers of deaths from lung cancer according to duration of employment, which was especially evident when 20 years or more of latency had elapsed. In the group with 20 years or more of both duration and latency, an SMR of 2.48 [95% CI, 1.19–4.56] (10 deaths) was recorded. The results for respiratory cancer were confirmed by using incidence data (SIR, 1.55). [The Working Group noted that the number of incident cases was not reported.] An indirect adjustment for smoking was made using the data from the questionnaire: The authors reported that smoking could not completely explain the excess of lung cancer. When an internal comparison of job categories was made with regard to lung cancer, an SMR of 2.83 [95% CI, 0.58–8.27] (three deaths) was found for drying/shipping, whereas no increase was found for workers exposed to chemical/fertilizer.

Hagmar *et al.* (1991) conducted a historical cohort study on workers employed in a Swedish fertilizer factory. The factory produced superphosphate (raw phosphate treated with a mixture of sulfuric acid and phosphoric acid) from its foundation in 1882 until 1937; from 1907, sulfuric acid was also produced. Production of PK fertilizers (mainly superphosphate and potash) began in 1937, and that of phosphoric acid in 1940; production of nitrogen-containing fertilizers began in 1963. Two cohorts were assembled: 'nitrate fertilizer workers', 2131 men who had been employed in the factory for three months or longer during 1963–85 (these were omitted from consideration here); and 'other fertilizer workers', 1236 men who had been employed for three months or longer during 1906–62 but not after 1962. Follow-up for cancer incidence was carried out for the period 1958–86 through the national Swedish and southern Swedish regional tumour registries. Expected numbers of tumours were calculated from county rates, taking into consideration calendar year and age. A total of 128 cancer cases was observed in the 'other fertilizer workers' cohort (SIR, 0.97; 95% CI, 0.81–1.16). Significant excesses were seen of cancer of the respiratory tract (29 cases; SIR, 1.52; 95% CI, 1.03–2.20) and of cancer of the lung and pleura (25 cases; SIR, 1.51; 95% CI, 0.99–2.25); the remaining four cases were nasal and laryngeal cancers (RR, 1.6; 95% CI, 0.4–4.1). The elevated risks remained when analyses were restricted to 10 or more years of latency. Nine cancers of the oral cavity and pharynx were seen (SIR, 1.76; 95% CI, 0.81–3.35).

2.2.8 *Lead battery (accumulator) manufacture*

Cohort studies of workers employed in lead–acid battery manufacture have been reviewed previously (IARC, 1980, 1987). The results of a cohort study of 7032 US workers in six lead production facilities and 10 battery plants, first reported by Cooper and Gaffey (1975), were reported by Cooper *et al.* (1985) for 34 years of follow-up (1947–80). Of 4519 workers who had been exposed in the battery plants for at least one year, 1718 had died (82 without a death certificate). Total mortality was greater than in the US white male population (SMR, 1.07; 95% CI, 1.02–1.12), and there was a significant excess of deaths due to all malignant neoplasms (344 deaths; SMR, 1.13; 95% CI, 1.02–1.26). The excess was due mainly to more deaths than expected from stomach cancer (34 deaths; SMR, 1.68; 95% CI, 1.16–2.35) and from lung cancer (109 deaths; SMR, 1.24; 95% CI, 1.02–1.50). An examination of cancer mortality in terms of cumulative years of employment in the battery plants showed no evident trend for either stomach or lung cancer.

Long-term employees who received a pension from four lead–acid battery companies in the United Kingdom were studied by Malcolm and Barnett (1982). A total of 1898 subjects (1644 men) were followed up from 1925 through 1976. In addition, a list of all 553 employees who had died while still employed in the largest of the four factories was available. Death certificates were obtained mostly from the company pension scheme. National statistics provided reference numbers. Workers were classified into three groups of potential occupational exposure to lead on the basis of their jobs. SMRs were calculated for the cohort of pensioners and proportionate mortality rates (PMRs) for the workers who had died while still employed. There were 754 deaths from all causes in male pensioners (SMR, 0.99 [95% CI, 0.92–1.06]). Mortality during service from all malignant neoplasms was slightly elevated (136 observed; PMR, 1.15 [95% CI, 0.96–1.06]), particularly among people in the highest category of lead exposure. [The Working Group noted that exposure to lead may not be correlated with exposure to acid and that incomplete reporting of the follow-up of the total cohort and emphasis on retirees limit the usefulness of the study.]

2.2.9 *Other industries*

Cumulative exposure to sulfuric acid was calculated in a study of deceased workers from a US copper smelter (Rencher *et al.*, 1977), described in detail in the monograph on sulfur dioxide (p. 159). Workers who died of lung cancer had higher indices of exposure to arsenic, lead, sulfur dioxide and sulfuric acid than workers who died of non-respiratory cancer.

In a follow-up study of workers with potential exposure to acrylamide in four chemical plants in USA and the Netherlands, Collins *et al.* (1989) reported an excess of lung cancer at one of the facilities studied. The excess was due partly to an increased number of lung cancer deaths (11 deaths) observed among men who had worked in a muriatic acid [hydrochloric acid] department. [The Working Group noted that the expected numbers were not reported.]

2.3 Case–control studies

Results of case–control studies are summarized in Table 17 (p. 97).

2.3.1 *Laryngeal cancer*

A case–control study of workers at the refinery and chemical plant in Baton Rouge, LA (USA), previously studied by Lynch *et al.* (1979), was designed to examine the association between upper respiratory cancers (including the oropharynx) and exposure to sulfuric acid (Soskolne *et al.*, 1984). Fifty incident cases, diagnosed between 1944 and 1980, were ascertained from company medical records, social security administration records and the county cancer registry and matched to 175 controls for sex, age, race, duration of employment and year of first employment. Only workers who had been employed for one or more years were included. Occupational exposures to sulfuric acid and several other substances were estimated for the job of each subject by the plant industrial hygienist. The odds ratios for cancer were increased for workers with exposure to sulfuric acid at moderate (2.2; 95% CI, 0.78–6.36) and high levels (4.0; 95% CI, 1.26–12.7) compared with the no/low category, using the mean grade exposure measure and adjusting for the effects of tobacco, previous history of ear, nose and throat diseases and alcoholism. The odds ratios were higher when laryngeal cancer cases were considered (4.6; 0.83–25.35; and 13.4; 2.08–85.99, respectively). Asbestos, nickel and wood dust were not related to the risk for laryngeal cancer. Industrial hygiene information was not available about the presence of dialkyl sulfates in all units and processes, so this exposure could not be included in the analysis; however, an analysis excluding workers in both the ethanol and isopropanol units and an analysis of workers exposed only in the weak-acid process gave odds ratios and exposure–response relationships of the same order of magnitude.

Table 16. Cohort studies of workers in industries which involve potential exposure to inorganic acid aerosols

Reference (country)	Number of workers	Larynx			Lung			Comments
		N[a]	RR[b]	95% CI	N[a]	RR[b]	95% CI	
Isopropanol manufacture								
Weil *et al.*, 1952 (USA)	182 (71 exposed for >5 years)	1[c]	-	-	1	-	-	Method of enumeration of cohort unclear. Four sinonasal cases represent an apparent, large excess (2 dead, 2 surviving). Cases of cancer found in workers exposed >5 years
Alderson & Rattan, 1980 (UK)	262				2	0.78	[0.09-2.8]	Increased risks for cancers of kidney (6.5 [0.8-23.3]) and brain (16.7 [2.0-60.2]) based on 2 cases each and sinonasal cancer (50.0 [0.65-278.2]) based on 1 case
Enterline, 1982 (USA)	433 (125 also exposed to epichlorohydrin)				4	2.48	[0.67-6.36]	Workers also exposed to epichlorohydrin
					3	0.69	[0.14-2.02]	Workers not exposed to epichlorohydrin
Synthetic ethanol and isopropanol manufacture by the strong-acid process								
Lynch *et al.*, 1979 (USA)	335	4[c]	5.04	[1.36-12.90]				Isopropanol + ethanol manufacture. Assumed to be due to diethyl sulfate
Teta *et al.*, 1992 (USA)	1031	2	[2.0]	[0.22-7.22]	22	[0.94]	[0.59-1.43]	Ethanol, 1930-68, isopropanol, 1928-49, both by strong-acid process
Pickling and other acid treatment of metals								
Mazumdar *et al.*, 1975 (USA)								
Batch pickling and sheet dryers					0[d]	-	-	
Coating					4[d]	[1.43]	[0.4-3.66]	
Continuous pickling and electric cleaning					0[d]	-	-	
Sheet finishing and shipping					19[d]	1.22	[0.7-1.9]	

Table 16 (contd)

Reference (country)	Number of workers		Larynx			Lung			Comments
			N^a	RR^b	95% CI	N^a	RR^b	95% CI	
Pickling and other acid treatment of metals (contd)									
Mazumdar *et al.*, 1975 (USA) (contd)									
Stainless annealing, pickling and processing						2^d	[3.3]	[0.4–12.0]	
Tin finishing and shipping						2	[0.56]	[0.1–2.01]	
Ahlborg *et al.*, 1981 (Sweden)	110		3^c		(Exp: 0.06)	1		(Exp: 0.60)	
		> 10 years' induction time	3^c		(Exp: 0.05)	1		(Exp: 0.50)	
Beaumont *et al.*, 1987 (USA)	1165	Any acid	2	1.93	0.23–6.99	35	1.64	1.14–2.28	SMR = 1.85 (1.25–2.64) for any acid and SMR = 1.93 (1.10–3.13) for sulfuric acid daily with ≥ 20 year latency. Adjustment for smoking in some analyses. Associations lower when comparisons made to a steelworker population
		Sulfuric acid only				19	1.39	[0.84–2.17]	
		Sulfuric acid, daily				18	1.58	[0.94–2.50]	
		Mixed sulfuric and other acids				7	1.92	[0.77–3.95]	
		Other acid only (primarily hydrochloric)				9	2.24	[1.02–4.25]	
Steenland & Beaumont, 1989 (USA)	1165	20 years since first exposure				41 NR	1.36 1.50	0.97–1.84 1.05–2.27	Extension of cohort of Beaumont *et al.* (1987). RRs indirectly adjusted for smoking. No increase in risk with duration of employment
Steenland *et al.*, 1988 (USA)	879		9^c (5 dead, 4 alive)	2.3	[1.05–4.36]				RRs adjusted for smoking and alcohol. Four cases exposed to sulfuric acid only, three to mixed acids, and two only to acids other than sulfuric (primarily hydrochloric).

Table 16 (contd)

Reference (country)	Number of workers		Larynx			Lung			Comments
			N[a]	RR[b]	95% CI	N[a]	RR[b]	95% CI	
Sulfuric acid manufacture									
Thiess *et al.*, 1969 (Germany)	259					8	[6.7]	-	Crude ratio, not age-adjusted. One case was an office worker.
Englander *et al.*, 1988 (Sweden)	400					5[d]	2.00	[0.50–4.67]	SMR = 1.83 [95% CI, 0.50–4.69] for ≥5-year latency. Excess of bladder cancer
Soap and detergent manufacture									
Forastiere *et al.*, 1987 (Italy)	361		1	2.30	0.09–11.43	5	1.69	0.55–3.86	Nickel potential confounder
			5[c]	[6.94] [3.47]	[2.25–16.2] [1.13–8.10]				Two SIRs according to reference population
Nitric acid manufacture									
Hilt *et al.*, 1985 (Norway)	190	All				6[c]	2.4	0.92–5.4	Exposure to nitric acid not qualified
		Maintenance				3[c]	5.0	1.03–4.61	One pleural mesothelioma included; asbestos a potential confounder
		Production				3[d]	[1.6]	[0.31–4.61]	
Phosphate fertilizer manufacture									
Checkoway *et al.*, 1985a,b (USA)	17 601 white men		3	0.66	[0.14–1.93	117	1.22	[1.01–1.46]	RR based on US male rates. Trend of lung cancer risk with latency. No excess of lung cancer among non-whites using local reference rates. No trend with duration of employment in departments with exposure to sulfuric or phosphoric acids. Racon decay products a potential confounder.
	4 722 non-white men		1	0.42	[0.006–2.34]	46	1.24	[0.91–1.65]	

Table 16 (contd)

Reference (country)	Number of workers		Larynx			Lung			Comments
			N[a]	RR[b]	95% CI	N[a]	RR[b]	95% CI	
Phosphate fertilizer manufacture (contd)									
Stayner *et al.*, 1985 (USA)	3199	All	0		(Exp: 0.43)	10	1.13	[0.54–2.08]	Trend with duration of employment and length of follow-up among blacks, not among whites. Radon decay products a potential confounder.
		Blacks				5	1.82	[0.59–4.26]	
Block *et al.*, 1988 (USA)	2607 white men		2	1.91	[0.23–6.90]	37	1.62	[1.14–2.23]	Trend in risk of lung cancer death or incidence with duration of employment among long-term workers. No major confounding by smoking; radon decay products a potential confounder.
	840 black men		0			9	1.04	[0.48–1.97]	
Hagmar *et al.*, 1991 (Sweden)	1236		[4][e]	[1.6]	[0.4–4.1]	25[f]	1.51	0.99–2.25	SMR = 1.50 (0.98–2.26) with 10-year latency
Lead battery (accumulator) manufacture									
Cooper *et al.*, 1985 (USA)	4519		6	1.28	0.47–2.80	109	1.24	1.02–1.50	No trend in lung cancer risk with duration of employment. Stomach cancer: SMR = 1.68 (1.16–2.35)
Other industries									
Collins *et al.*, 1989 (USA)	8854					161	1.32	[1.1–1.5]	Excess lung cancer in two groups in one facility, including muriatic acid department (11 cases). No expected number of deaths given

RR, relative risk; CI, confidence interval; NR, not reported

[a] Number of events; deaths from specified cancer except where noted otherwise

[b] Estimate

[c] Incident case

[d] Respiratory tract

[e] Sinonasal and larynx combined

[f] Lung and pleura combined

A case–control study of laryngeal cancer was conducted at the Institute of Oncology in Gliwice, Poland (Zemla *et al.*, 1987), comprising 328 histologically confirmed laryngeal cancer cases among men referred for the first time to the hospital for treatment during 1980–84. Controls were 656 individuals with no neoplastic disease. Information about occupational and life-style factors was derived from questionnaires. The authors reported increased odds ratios for manual workers 'constantly' exposed to vapours of sulfuric acid, hydrochloric acid and nitric acid (relative risk [RR], 4.27; $p < 0.001$, based on 11 exposed cases). A nonsignificantly increased risk (RR, 1.66) was observed for manual workers 'constantly' exposed to dust and vapours, based on 20 exposed cases. [The Working Group noted that the methods were inadequately described.]

A population-based case–control study was conducted on the Texas Gulf Coast, USA (Brown *et al.*, 1988). Cases were 183 incident cases (136 living, 47 dead) of squamous-cell carcinoma of the larynx diagnosed during 1975-80 among white men aged 30–79 years; 250 controls (179 living, 71 dead) were frequency matched. Interviews were completed for 69.5% of living and 67.5% of dead cases and for 62.8% of dead controls, 60.9% of controls less than 65 years old and 85.7% of controls over 65 years of age. Exposure assessment was based on an industrial hygienists's evaluation of complete job histories. A significantly increased risk was found (odds ratio, 2.11; 95% CI, 1.17–3.78) for any exposure in metal fabricating. For all workers with potential exposure to sulfuric acid, the odds ratio was 0.76 (95% CI, 0.42–1.35). Both odds ratios were controlled for tobacco and alcohol intake. [The Working Group noted the relatively low participation rates.]

In a population-based case–control study, 183 incident male cases of histologically confirmed carcinoma of the larynx diagnosed between 1977 and 1979 in southern Ontario, Canada, and 183 controls matched for sex, age and neighbourhood were compared for exposure to sulfuric acid (Soskolne *et al.*, 1992). (The response rate was 79% for cases; 77.5% of controls agreed to participate at initial approach [Burch *et al.*, 1981]). Detailed work histories and information on tobacco and alcohol use were obtained by personal interview. Concentration and frequency of exposure to sulfuric acid for each job were estimated by the same method described by Siemiatycki (1991) (see below) and were assessed independently using three four-point scales; the degree of confidence of the industrial hygienist in the reliability of these assessments was included in the exposure scheme. The product of these measures for each job was squared and then multiplied by the time spent in that job, and this value was summed over all jobs. This total was then divided by the total time of exposure to the concentration and/or frequency scores of 1 or more to calculate 'average exposure level'. Conditional logistic regression analysis using two categories of exposure and controlling for tobacco and alcohol use resulted in an odds ratio of 3.04 (95% CI, 1.67–5.53). Omitting exposures in the five years prior to diagnosis and including only the most specific exposure scale resulted in a significant dose–response effect, with an odds ratio of 2.52 (95% CI, 0.80–7.91) at the lowest level and 6.87 (95% CI, 1.00–47.06) at the highest. Asbestos was not a significant confounder.

2.3.2 *Multiple myeloma*

A population-based case–control study of multiple myeloma addressed the potential carcinogenicity of several toxic substances, including acids and fertilizers (Morris *et al.*, 1986). Cases were identified through cancer registries serving four areas in the USA. For 698 cases (89% of those recruited initially) diagnosed between 1977 and 1981, either a direct (68%) or a next-of-kin interview was available. Controls were chosen randomly from among residents of the areas inhabited by the cases under study; 1683 controls (83%) were interviewed (99% in person). After excluding interviews with next-of-kin of cases, the odds ratio (adjusted for several potential confounders) was somewhat increased for exposures to acids (1.5; 95% CI, 0.8–2.8); when all subjects were considered, the ratio was 1.0 (95% CI, 0.6–1.9).

2.3.3 *Cancers at multiple sites*

A population-based case–control study of cancer included histologically confirmed cases of cancer at 11 major sites (not including larynx), newly diagnosed between 1979 and 1985 among male residents of Montréal, Canada, aged 35–70, ascertained in 19 major hospitals (Siemiatycki, 1991). With a response rate of 82%, 3730 cancer patients were successfully interviewed. For each site of cancer analysed, two control groups were used, giving rise to two separate sets of analyses and results: one control group selected from among cases of cancer at the other sites studied (cancer controls) and the other consisting of 533 population controls representing those successfully interviewed from an age-stratified sample of the general population (response rate, 72%). The interview was designed to obtain detailed lifetime job histories and information on potential confounders. Each job was reviewed by a trained team of chemists and hygienists who translated jobs into occupational exposures. Of these, 293 of the most common occupational substances were then analysed as potential risk factors in relation to each site of cancer included. Cumulative exposure indices were created for each substance, on the basis of duration, concentration, frequency and the degree of certainty in the exposure assessment itself, and these were analysed at two levels: 'any' and 'substantial' exposure; the latter is a subset of 'any'. Analyses were repeated for a French-Canadian subset, comprising about 60% of the total sample and providing a population that is relatively homogeneous from both a genetic and social perspective, in order to eliminate important sources of confounding and effect modification. Among the substances on the checklist was the general category 'inorganic acid solutions', described as mainly solutions of hydrochloric, sulfuric and nitric acids, to which 13% of the entire study population had been exposed at some time (i.e., lifetime exposure prevalence). Unless otherwise stated, the results quoted are based on cancer controls and the 'any' exposure level. For inorganic acid solutions, there were two significant associations: a RR of 2.0 for oat-cell carcinoma of the lung (33 cases; 90% CI, 1.3–2.9) and a RR of 1.7 for cancer of the kidney (32 cases; 90% CI, 1.2–2.4). The RRs at the 'substantial' levels of exposure were about the same but were based on fewer cases and thus had wider CIs. No excess risk for other histological types of lung cancer was seen, and the RR for all lung cancers combined was 1.2 for any exposure to inorganic acid solutions (129 cases; 90% CI, 1.0–1.6) and 1.1 (0.7–1.6) for substantial exposure. When the category of sulfuric acid alone was analysed, 9% of the entire study population had been exposed at some time. Some evidence of an association with exposure to sulfuric acid was found for all lung cancers and for oat-cell carcinoma of the lung in the French-Canadian subset of the population and for squamous-cell carcinoma of the lung in the whole population. An elevated RR of 2.2 was found for oesophageal cancer (15 cases; 90% CI, 1.3–3.6) in the whole population, again with no indication of higher risk at the substantial exposure level. There was weak evidence of an excess risk for kidney cancer, restricted to the French-Canadian subset of the study population with substantial exposure (four cases; RR, 2.5; 90% CI, 1.0–6.1).

3. Studies of Cancer in Experimental Animals

No data were available to the Working Group.

4. Other Relevant Data

4.1 Absorption, distribution, metabolism and excretion

4.1.1 *Humans*

The impact of an inhaled acidic agent on the respiratory tract depends on a number of interrelated factors which include whether it is a gas or an aerosol; particle size, small particles being more able to penetrate deeply into the lung (Martonen *et al.*, 1985; Jarabek *et al.*, 1989; US Environmental Protection Agency, 1989b); water solubility, agents of higher solubility being more likely to be deposited in the nose and mouth; free hydrogen ion concentration; rate and breathing pattern; and the buffering capacity of the airways and of the local deposition site (Utell *et al.*, 1989). The specific anion may modulate acute effects directly or indirectly. The impact also depends upon the presence of any other chemicals that are carried along with the aerosol particle.

Given the general lack of information on the particle size of aerosols of acids during occupational exposures, it is difficult to clarify the principal deposition site within the respiratory tract. For example, 90% of an aerosol of sulfuric acid (mass median aerodynamic diameter of particles, 5 μm) to which lead–acid battery workers are exposed would be deposited in the extrathoracic portion of the respiratory tract, whereas only 50% of an aerosol with a 2-μm particle size would be deposited in that portion of the respiratory tract. This relationship of size to deposition makes estimation of the changes in pH of the mucus problematic, as diffuse deposition challenges the buffering capacity much less than does deposition of large particles at local sites (Gamble *et al.*, 1984a; Jarabek *et al.*, 1989).

Using an average particle size of 1 μm and exposure concentrations of 0.4–1.0 mg/m^3, Amdur *et al.* (1952) showed that 77% of inhaled sulfuric acid was retained in the airways of exposed human subjects. Martonen *et al.* (1985) calculated the growth of $\leq$ 1-μm particles of several inorganic acids within the respiratory tract and found that it depended on humidity, particle size, respiratory characteristics and the hygroscopic nature of the particle.

In the moist environment of the respiratory tract, sulfur trioxide reacts instantaneously with water to form sulfuric acid (see Annex, section 3.2, p. 123); therefore, the toxicology of sulfur trioxide would be expected to be the same as that of sulfuric acid. Ammonia produced by the respiratory tract can partially neutralize the acidity of acid aerosols (Larson *et al.*, 1977; Utell *et al.*, 1989) in the mucous lining of the respiratory tract. Inhalation studies of

Table 17. Case–control studies of risks associated with exposure to inorganic acid aerosols

Reference (country)	Study population	Definition of exposure (source of data)		Exposed cases	OR	95% CI	Comments
Laryngeal cancer							
Soskolne *et al.*, 1984 (USA)	Nested in cohort of workers in refinery and chemical plant (50 upper respiratory cancers of which 30 laryngeal; 175 controls)	Average sulfuric acid (industrial hygienist's evaluation based on work history from personnel records)	'Moderate'	–	4.6	0.83–25.4	Adjusted for tobacco smoking and history of alcoholism and ear, nose and throat diseases. Matched analysis; number of discordant sets not available
			'High'	–	13.4	2.08–86.0	
Zemla *et al.*, 1987 (Poland)	(328 cases; 656 controls)	Sulfuric, hydrochloric, nitric acids (interview included 'occupational factors')		11	4.27	Not reported	Lack of details on methods; insufficient data to calculate CIs; $p \leq 0.001$
Brown *et al.*, 1988 (USA)	Population-based (183 cases; 250 controls)	Sulfuric acid (industrial hygienist's evaluation based on complete work history from interview)		22	0.76	0.42–1.35	Adjusted for smoking and alcohol consumption; low response rate
Soskolne *et al.*, 1992 (Canada)	Population-based (183 cases; 183 controls)	Sulfuric acid mists (job exposure matrix; full occupational history from interview)		134	3.04	1.67–5.53	Trend with level of exposure. Similar results with more specific definition of exposure.
Multiple myeloma							
Morris *et al.*, 1986 (USA)	Population-based (698 cases; 1683 controls)	Acids (self-reported by interview)	Direct interviews	–	1.5	0.8–2.8	Adjusted for age, sex and race
			Both direct and next-of-kin interviews	–	1.0	0.6–1.9	
Multiple sites							
Siemiatycki, 1991 (Canada)	Population-based (lung cancer: 857 cases, 1360 controls; kidney cancer: 177 cases, 2481 controls; oesophageal cancer: 99 cases, 2546 controls)	Inorganic acid solutions	Lung				No excess cancers of oesophagus, stomach, colon, rectum, pancreas, prostate or bladder, skin melanoma or non-Hodgkin's lymphoma
			Any exposure	129	1.2	1.0–1.6[a]	
			Substantial exposure	32	1.1	0.7–1.6[a]	

Table 17 (contd)

Reference (country)	Study population	Definition of exposure (source of data)		Exposed cases	OR	95% CI	Comments
Multiple sites (contd)							
		Inorganic acid solutions (contd)	Kidney				
			Any exposure	32	1.7	1.2–2.4[a]	
			Substantial exposure	11	1.8	1.0–3.1[a]	
		Sulfuric acid	Lung				No excess cancers of stomach, colon, rectum, pancreas, kidney, prostate or bladder, skin melanoma or non-Hodgkin's lymphoma
			Any exposure	60[b]	1.2	0.8–1.9[a]	
			Substantial exposure	8[b]	2.9	0.8–10.4[a]	
			Oat-cell (any exposure)	16[b]	1.7	1.0–2.9[a]	
			Squamous-cell (any exposure)	38	1.5	1.0–2.4[a]	
			Oesophagus				
			Any exposure	15	2.2	1.3–3.6[a]	
			Substantial exposure	3	2.1	0.8–5.8[a]	

OR, odds ratio; CI, confidence interval

[a] 90% CI

[b] French Canadians only

ammonium sulfate may therefore be relevant to an assessment of the carcinogenicity of inhaled sulfuric acid.

The breathing pattern (e.g., mouth *versus* nose breathing with normal augmentation through the mouth) also influences deposition. The dose deposited regionally below the nasopharynx is higher for mouth breathers for all particle sizes. The effect of mouth breathing is most pronounced in increasing deposition in the oropharynx, larynx and upper trachea (Jarabek *et al.*, 1989).

4.1.2 *Experimental systems*

Generally, similar information is available for animals and humans. Regional deposition of sulfuric acid aerosols in experimental animals is thus also dependent on particle size (e.g., Dahl *et al.*, 1983). Animal species differ from humans with regard to the dimensions and architecture of the respiratory tract, and deposition patterns of aerosols vary accordingly (Jarabek *et al.*, 1989). Ammonia production by the respiratory tract is important in partial neutralization of acid aerosols, but larger particles are neutralized less efficiently than smaller particles (e.g., Larson *et al.*, 1982).

4.2 Toxic effects

4.2.1 *Humans*

The toxic effects of acid aerosols, including those containing sulfuric acid, have been reviewed (Fouts & Lippmann, 1989; US Environmental Protection Agency, 1989b). Of the acidic mists, sulfuric acid has been studied most extensively. As for deposition, the toxicity of acid mists to the lung depends in part on aerosol size, smaller particles penetrating more deeply into the lung (Lippmann *et al.*, 1987).

Acids are highly corrosive and irritating and give rise to local effects on the skin, eye and other mucous epithelia when there is direct exposure to sufficient concentrations (see also monograph on hydrochloric acid).

Sulfur dioxide and related acid mists of sulfuric acid have caused respiratory irritation, bronchitis and death (WHO Working Group, 1986; WHO, 1987; American Thoracic Society, 1991) (see also the monographs on sulfur dioxide and hydrochloric acid).

Concern about the health effects of acidic aerosols, and particularly sulfuric acid and acid sulfates, was accentuated by the episodes of smog in London in the 1950s and 1960s, during which thousands more deaths than expected were recorded. People at particular risk were those with pre-existing cardiovascular and pulmonary disease. Similar gas–aerosol complexes have been responsible for acute and chronic lung disease, including potentiation of respiratory tract infections and chronic bronchitis in geographical areas where there is significant air pollution from stationary sources of fossil fuel combustion (Thurston *et al.*, 1989). Although sulfuric acid is only one component of these complexes, it has been suggested that hydrogen ion concentration, presumably primarily reflecting sulfuric and nitric acids, is correlated with bronchitic symptoms in children (Speizer, 1989; US Environmental Protection Agency, 1989b). Levels of sulfate and fine particles may also be better predictors of mortality than are concentrations of total suspended particles or inhalable particles (Özkaynak & Thurston, 1987).

The historical cohort study of mortality among 22 323 workers in the Florida phosphate industry, described on pp. 85–86 (Checkoway *et al.*, 1985a), showed increased mortality from emphysema (31 cases; SMR = 1.48; $p < 0.05$). No clear trend with length of employment or years since first employment was seen, but the excess mortality was more pronounced among workers first hired before 1940 (9 cases) than among those hired after 1940 (22 cases). [The Working Group noted, as did the authors, that this finding is difficult to interpret in the light of the many exposures of these workers, the absence of information on tobacco smoking and variation in the diagnoses of chronic respiratory diseases.]

Airway mucus has a high buffering capacity and protects the epithelial cells of the respiratory mucous membranes. Its viscosity depends on pH, and acidified mucus of increased viscosity diminishes lung function. People who have acidic mucus with a low protein concentration (e.g., people with infections or inflammations and some asthmatics) may be at high risk when exposed to acids (Holma, 1989).

Estimates of the pH of mucus range from 6.5 to 7.5, with a mean of approximately 6.9. [The Working Group noted that chemical composition, and therefore the pH of mucus, vary within the respiratory tract and can be changed by sampling techniques.] The US Environmental Protection Agency (1989b) has estimated that exposure to sulfuric acid at 390–780 μg [1300 μg/m^3] for 30 min at a ventilation rate of 20 litres/min and 50% deposition (for a particle size of 2 μm) would lower the pH of the mucus in the tracheo-bronchial region by approximately 1 unit. This calculation assumes that the distribution of sulfuric acid is uniform; non-uniform distribution would alter the change in pH in specific regions. The calculation does not take into consideration neutralization of acid in the airways by ammonia.

Dental erosion has been observed as a result of industrial exposure to acid mists. Bruggen Cate (1968) studied dental erosion in 555 workers from several industries in the United Kingdom where acid processes (pickling, galvanizing and battery manufacture) were used. Control subjects were selected from among workers in other departments in the same firms where acid was not used. Exposure to acids was not measured. The prevalence of dental erosion was highest among battery formation workers and lower among picklers. A similar association was seen in a sample of 186 workers from battery factories in Finland (Tuominen *et al.*, 1989). Various degrees of dental erosion were seen in 90% of picklers in a zinc galvanizing plant in the Netherlands; the threshold limit value for hydrochloric acid (7 mg/m^3) was exceeded for 27% of the working time (Remijn *et al.*, 1982).

Controlled human exposures to relatively high levels of sulfuric acid resulted in acute symptoms and other findings suggestive of bronchoconstriction (Balmes *et al.*, 1989). Effects have generally not been observed in healthy adults exposed acutely to levels of less than 500 μg/m^3 over a broad range of particle sizes, although delayed symptomatology (mild throat irritation and increased carbachol bronchorestrictor response) was noted after exposure to 450 μg/m^3 for 4 h while exercising moderately (Utell, 1985). Concentration (0, 500, 1000 and 2000 μg/m^3)-related increases in upper respiratory symptoms (cough) without change in pulmonary function have also been noted (Avol *et al.*, 1988). Exercising asthmatics were reported to be highly responsive (in terms of decreased forced expiratory volume in 1 sec) to a low level of sulfuric acid (100 μg/m^3) (Koenig *et al.*, 1989).

Acute exposure of human volunteers to 100 μg/m³ of sulfuric acid resulted in increased mucociliary clearance of particles from the large proximal airways; at higher levels (1000 μg/m³), the opposite occurred. Clearance from the distal airways was reduced at both levels (Leikauf *et al.*, 1984).

The acute and chronic effects of sulfuric acid were studied in five lead–acid battery plants. Personal monitoring of 225 workers revealed mean exposures to sulfuric acid of 0.18 mg/m³ (range, 0.08–0.35 mg/m³) at an average mass median aerodynamic diameter of close to 5 μm. No difference was noted in acute symptoms between groups exposed to high (> 0.3 mg/m³) and low (< 0.07 mg/m³) levels of sulfuric acid, although eye irritation and cough were more prevalent in the groups with higher exposure. The possibility that workers became acclimatized to the acute effects of sulfuric acid was considered: neither short-term nor long-term changes in pulmonary function (as measured by spirometry) were observed, and the prevalence of respiratory symptoms was not related to cumulative acid exposure. Dental etching and erosion occurred about four times more frequently in the group exposed to high levels of acid (Gamble *et al.*, 1984a,b).

Other health effects have been reported in industries in which acidic mists occur, which have been attributed to other pollutants. For instance, haematological effects seen in the lead battery industry have been presumed to be due to lead (IARC, 1980).

4.2.2 *Experimental systems*

In donkeys (Lippmann *et al.*, 1982) and in rabbits (Schlesinger, 1990), repeated exposures to sulfuric acid at levels that initially increased mucociliary clearance of particles led over time to decreased clearance, indicating chronic effects. Sulfuric acid significantly reduced the phagocytic capacity of alveolar macrophages in rabbits exposed by inhalation to $\geq$ 1000 μg/m³ for 1 h per day for five days (Schlesinger *et al.*, 1990).

The alveolar phagocytotic response *in vitro* was related linearly to exposure *in vitro* to H^+, whereas the response *in vivo* was not (Schlesinger *et al.*, 1990).

Changes in particle bronchial clearance and an increased number of mucus secretory cells were observed in rabbits exposed to sulfuric acid at 250 μg/m³ for 1 h per day on five days per week for up to 12 months; no change in the pulmonary tissues was observed by routine histological procedures (Gearhart & Schlesinger, 1986; Schlesinger & Gearhart, 1986; Gearhart & Schlesinger, 1989). Sulfuric acid may induce hyperresponsiveness of the airways in exposed rabbits (Gearhart & Schlesinger, 1986).

Long-term, continuous exposure to sulfuric acid mist had no effect in three groups of 100 guinea-pigs exposed for 52 weeks to filtered air (control), to 0.10 mg/m³ sulfuric acid with a particle size of 2.78 μm mass median aerodynamic diameter or to 0.08 mg/m³ sulfuric acid with a particle size of 0.84 μm. In a similar study, five groups of nine cynomolgus monkeys were exposed continuously for 78 weeks to sulfuric acid. Deleterious effects were seen on pulmonary function and respiratory histology, depending on the concentration and particle size of the sulfuric acid. Effects were particularly prominent in monkeys exposed to 4.79 mg/m³ with a particle size of 0.73 μm mass median aerodynamic diameter. At 0.48 mg/m³ (0.54 μm) and 0.38 mg/m³ (2.15 μm), only minimal effects were noted (Alarie *et al.*, 1973).

4.3 Reproduction and developmental effects

4.3.1 *Humans*

No data were available to the Working Group.

4.3.2 *Experimental systems*

Groups of 35–40 CF-1 mice and 20 New Zealand rabbits were exposed *via* inhalation to aerosols containing sulfuric acid (purity, 95.7%) at 0, 5 or 20 mg/m^3 for 7 h per day on days 6–15 or 6–18 of gestation, respectively. The count medium diameters of particles in the chambers were 0.4, 1.6 and 2.4 μm in the control, low-dose and high-dose groups. Animals were deprived of food and water during exposure. Mouse fetuses were examined on day 18 and rabbit fetuses on day 29 of gestation. In dam mice, body weight was not significantly lower than that of controls; food consumption was reported to be decreased during the first few days of exposure at 20 mg/m^3 but not at 5 mg/m^3; no alteration was noted in respiratory tract histology. In dam rabbits given the high dose, body weight was significantly reduced in the early part of the exposure period, and histological examination of the respiratory tract showed a dose-related increase in the incidence of subacute rhinitis and tracheitis. No significant effect on embryonic viability or growth was noted in either species, and no dose-related morphological effect was seen in mouse fetuses. One case of a very rare defect (conjoined twinning) was seen in the litter of a mouse given the high dose. The only significant effect seen in rabbit fetuses was an increased incidence of 'small non-ossified areas in the skull bones' in the high-dose group (Murray *et al.*, 1979). [The Working Group noted that actual data were not given.]

4.4 Genetic and related effects (see also Table 18 and Appendices 1 and 2)

4.4.1 *Humans*

(*a*) *Sulfuric acid manufacture*

The frequencies of sister chromatid exchange, micronuclei and chromosomal aberrations in cultured lymphocytes from 40 workers exposed to sulfur dioxide in a sulfuric acid factory in Taiyuan City, northern China, were compared with those of 42 controls working and studying at a university situated in the same city as the factory, who were matched according to sex, age and smoking habits. The concentrations of sulfur dioxide in the factory varied irregularly from 0.34 to 11.97 mg/m^3 at the time of investigation. The mean number of sister chromatid exchanges/cell was 6.72 ± 0.22 for sulfur dioxide-exposed workers and 2.71 ± 0.31 for unexposed controls ($p < 0.01$); the mean frequency of micronuclei in cultivated lymphocytes was 0.168% in those from the workers and 0.071% for the control group ($p < 0.001$); and the mean frequency of severe types of chromosomal aberration (including rings, translocations and dicentrics) per 100 metaphases was 0.963% for the workers and 0.227% for controls ($p < 0.01$). No positive correlation was observed between the frequency of sister chromatid exchange, micronuclei or chromosomal aberrations and length of service of the workers. While there was no significant difference between smokers and nonsmokers with regard to the frequencies of sister chromatid exchange and chromosomal aberrations, smokers among both the workers and the control group had significantly more micronuclei than nonsmokers ($p < 0.001$) (Meng & Zhang, 1990a,b). [The Working Group noted that no information was provided on exposures other than to sulfur dioxide.]

(*b*) *Lead battery (accumulator) manufacture*

No data on exposure to acid mists were given in reports of studies of sister chromatid exchange or chromosomal aberrations in workers in lead battery manufacture (Grandjean *et al.*, 1983; Al-Hakkak *et al.*, 1986).

4.4.2 *Experimental systems*

Genotoxicity under extreme conditions of culture, including pH, has been reviewed (Scott *et al.*, 1991). No data were available on the genetic and related effects of exposures to acid mist in experimental systems; however, the effects of pH reduction have been investigated.

Low pH enhances the level of depurination of isolated DNA (Singer & Grunberger, 1983), and the fidelity of DNA replication and repair enzymes may be reduced by extremes of pH (Brusick, 1986). Low pH did not affect the frequency of point mutations in *Salmonella typhimurium* (with or without S9), *Escherichia coli*, *Neurospora crassa* or *Saccharomyces cerevisiae*, but it induced gene conversion in *S. cerevisiae*, chromosomal aberrations in *Vicia faba* root tips and a variety of mitotic abnormalities in sea urchin embryos and in offspring after treatment of sperm.

In mammalian systems, the genotoxic effects of low pH appear to be strongly enhanced by the presence of S9. Brusick (1986) reported that low pH induced chromosomal aberrations in Chinese hamster ovary cells only in the presence of S9. Morita *et al.* (1989), however, showed that in the same cells at low pH (5.5 or less) aberrations were also induced in the absence of S9, although S9 greatly enhanced the effect. No chromosomal effect was observed in rat lymphocytes incubated at pH 5.1, either with or without S9. Mutations have been reported in mouse lymphoma L5178Y cells exposed to low pH, both with and without S9, although the effect was only marginal (1.9 fold at pH 6.3) in the absence of S9. Reduction in pH from 7.35 to 6.70, achieved by lowering the concentrations of sodium bicarbonate in the medium, resulted in increased transformation frequency in Syrian hamster embryo cells.

5. Summary of Data Reported and Evaluation

5.1 Exposure data

Strong inorganic acids may be present in the work environment as mists, vapours or gases. The most prevalent acids are sulfuric, hydrochloric, nitric and phosphoric acids, which may be present in a wide variety of industries, including the extraction, fabrication and finishing of metal, fertilizer production, battery manufacture and various segments of the petroleum, chemical and petrochemical industries. Millions of workers worldwide are estimated to be potentially exposed to these acids.

Sulfuric acid is the most widely used of the strong inorganic acids. Average exposures to sulfuric acid mists in pickling, electroplating and other acid treatment of metals are frequently above 0.5 mg/m^3, while lower levels are usually found in the manufacture of

Table 18. Genetic and related effects of acidic pH

Test system	Result		Dose or pH	Reference
	Without exogenous metabolic system	With exogenous metabolic system		
SA0, *Salmonella typhimurium* TA100, reverse mutation	–	0	pH 3	Tomlinson (1980)
SA0, *Salmonella typhimurium* TA100, reverse mutation	–	–	pH 5.5	Cipollaro *et al.* (1986)
SA2, *Salmonella typhimurium* TA102, reverse mutation	–	–	pH 5.5	Cipollaro *et al.* (1986)
SA5, *Salmonella typhimurium* TA1535, reverse mutation	–	–	pH 3	Tomlinson (1980)
SA5, *Salmonella typhimurium* TA1535, reverse mutation	–	–	pH 5.5	Cipollaro *et al.* (1986)
SA9, *Salmonella typhimurium* TA98, reverse mutation	–	–	pH 5.5	Cipollaro *et al.* (1986)
SAS, *Salmonella typhimurium* TA97, reverse mutation	–	–	pH 5.5	Cipollaro *et al.* (1986)
ECR, *Escherichia coli*, (B/Sd–4/1,3,4,5) reverse mutation streptomycin^R	–	0	0.002–0.005%	Demerec *et al.* (1951)
ECR, *Escherichia coli*, (B/Sd–4/3,4) reverse mutation streptomycin^R	–	0	0.002–0.005%	Demerec *et al.* (1951)
SCG, *Saccharomyces cerevisiae*, gene conversion	+	0	pH 5.8	Nanni *et al.* (1984)
SCR, *Saccharomyces cerevisiae*, reverse mutation	–	0	pH 3.8	Nanni *et al.* (1984)
NCR, *Neurospora crassa*, reverse mutation	–	0	pH 3	Tomlinson (1980)
NCR, *Neurospora crassa*, reverse mutation	–	0	pH 3	Whong *et al.* (1985)
VFC, *Vicia faba*, chromosomal aberrations	+	0	pH 4.0	Bradley *et al.* (1968)
VFC, *Vicia faba*, chromosomal aberrations	+	0	pH 4.0	Zura & Grant (1981)
CIA, Chromosomal aberrations, *Sphaerechinus granularis* embryos, mitotic abnormalities	+	0	pH 6.0	Cipollaro *et al.* (1986)
CIA, Chromosomal aberrations, *S. lividus* embryos	+	0	pH 6.5	Pagano *et al.* (1985a)
CIA, Chromosomal aberrations, *Paracentrotus lividus* sperm, mitotic abnormalities	+	0	pH 6.5	Pagano *et al.* (1985b)
CIA, Chromosomal aberrations, *P. lividus* sperm, mitotic abnormalities	+	0	pH 5	Cipollaro *et al.* (1986)
CIA, Chromosomal aberrations, *S. granularis* sperm, mitotic abnormalities	+	0	pH 6.5	Cipollaro *et al.* (1986)
G5T, Gene mutation, mouse lymphoma L5178Y cells, *tk*	(+)	+	pH 6.0	Cifone *et al.* (1987)
CIC, Chromosomal aberrations, Chinese hamster CHO cells *in vitro*	–	+	pH 5.5	Brusick (1986)
CIC, Chromosomal aberrations, Chinese hamster CHO cells *in vitro*	+	+	pH 5.5	Morita *et al.* (1989)
CIR, Chromosomal aberrations, rat lymphocytes *in vitro*	–	–	pH 5.1	Sinha *et al.* 1989)
TFS, Cell transformation, Syrian hamster embryo cells, focus assay	+	0	pH 6.7	Le Boeuf & Kerckaert (1986)

lead–acid batteries and in phosphate fertilizer production. Exposure to sulfuric acid also occurs during its manufacture and during the production of isopropanol, synthetic ethanol and detergents. Hydrochloric acid is used in industries that involve acid treatment of metals, where occupational exposure levels to hydrochloric acid mists and gas are frequently above 1 mg/m^3. Exposures to hydrochloric acid may also occur during its synthesis and use in various industrial processes. Pickling and other acid treatments of metal may entail occupational exposures to nitric and phosphoric acids, but these occur less frequently than exposures to sulfuric and hydrochloric acids. Exposure to nitric acid also occurs during its manufacture and exposure to phosphoric acid in phosphate fertilizer production.

5.2 Human carcinogenicity data

An early study of isopropanol manufacture in the USA using the strong-acid process demonstrated an excess of nasal sinus cancer. Studies of one US cohort of workers in pickling operations within the steel industry showed excesses of laryngeal and lung cancer after smoking and other potential confounding variables had been controlled for. A Swedish study of a cohort of workers in steel pickling also showed an excess risk for laryngeal cancer. A nested case–control study of workers in a US petrochemical plant showed an elevated risk for laryngeal cancer among workers exposed to sulfuric acid. Of two population-based case–control studies in Canada, one of laryngeal cancer showed an increased risk for exposure to sulfuric acid, and one of lung cancer suggested an excess risk; the latter also suggested a risk associated with exposure to mixed inorganic acids. In all these studies, sulfuric acid mists were the commonest exposure, and positive exposure–response relationships were seen in two of the studies.

Additional supporting evidence was provided by one cohort study in the soap manufacturing industry in Italy, which showed an increased risk for laryngeal cancer. Studies of three US cohorts and one Swedish cohort in the phosphate fertilizer manufacturing industry showed excess lung cancer, but there was potential confounding from exposure to radon decay products in some cohorts.

5.3 Animal carcinogenicity data

No data were available to the Working Group.

5.4 Other relevant data

Acid mists containing particles with a diameter of up to a few micrometers will be deposited in both the upper and lower airways. They are irritating to mucous epithelia, they cause dental erosion, and they produce acute effects in the lungs (symptoms and changes in pulmonary function). Asthmatics appear to be at particular risk for pulmonary effects.

Significant increases in the incidences of sister chromatid exchange, micronucleus formation and chromosomal aberrations in peripheral lymphocytes were observed in a single study of workers engaged in the manufacture of sulfuric acid.

The studies reviewed examined the effects of pH values < 7 specifically. In cultured mammalian cells at pH 6.7 or below, cell transformation, gene mutation and chromosomal aberrations were induced. Mitotic abnormalities were induced in sea urchins and clastogenic effects in plants. Gene conversion was induced in yeast cells. No point mutation was observed in fungi, yeast or bacteria. Acid pH caused depurination of isolated DNA.

5.5 Evaluation[1]

There is *sufficient evidence* that occupational exposure to strong-inorganic-acid mists containing sulfuric acid is carcinogenic.

Overall evaluation

Occupational exposure to strong-inorganic-acid mists containing sulfuric acid *is carcinogenic to humans (Group 1).*

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[1] For definition of the italicized terms, see Preamble, pp. 26–29.

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ANNEX: CHEMICAL AND PHYSICAL PROPERTIES AND USES OF SULFURIC ACID AND SULFUR TRIOXIDE

1. Synonyms

Sulfuric acid

Chem. Abstr. Serv. Reg. No.: 7664-93-9
Replaced CAS Reg. Nos.: 119540-51-1; 127529-01-5
Chem. Abstr. Name: Sulfuric acid
IUPAC Systematic Name: Sulfuric acid
Synonyms: Battery acid; BOV; dihydrogen sulfate; dipping acid; electrolyte acid; hydrogen sulfate; matting acid; mattling acid; Nordhausen acid; oil of vitriol; sulphuric acid; vitriol brown oil

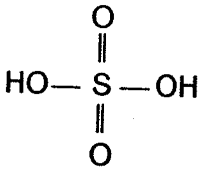
Sulfur trioxide

Chem. Abstr. Serv. Reg. No.: 7446-11-9
Chem. Abstr. Name: Sulfur trioxide
IUPAC Systematic Name: Sulfur trioxide
Synonyms: Sulfan; sulfuric anhydride; sulfuric oxide; sulfur oxide (SO_3); sulphur trioxide

Oleum

Chem. Abstr. Serv. Reg. No.: 8014-95-7
Chem. Abstr. Name: Sulfuric acid mixture with sulfur trioxide
Synonyms: Fuming sulfuric acid; sulfuric acid fuming

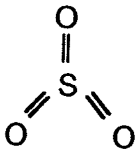
2. Structural and molecular data



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

H_2SO_4

Mol. wt.: 98.08



SO_3

Mol. wt.: 80.07

3. Chemical and physical properties

3.1 Sulfuric acid

Sulfuric acid is a strong acid with characteristic hygroscopic and oxidizing properties. The dehydrating effect of concentrated sulfuric acid is due to the formation of hydrates. Several hydrates have been identified in solid sulfuric acid; their presence explains the irregular variation with concentration of some of the physical properties of sulfuric acid. Known hydrates are $H_2SO_4 \cdot H_2O$ (corresponding to 84.5 wt% H_2SO_4); $H_2SO_4 \cdot 2H_2O$ (71.3 wt% H_2SO_4); $H_2SO_4 \cdot 3H_2O$ (64.5 wt% H_2SO_4); $H_2SO_4 \cdot 4H_2O$ (57.6 wt% H_2SO_4); and $H_2SO_4 \cdot 6H_2O$ (47.6 wt% H_2SO_4). Pure sulfuric acid is ionized to only a small extent, in accordance with the following equations:

$$2\,H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

and

$$2\,H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-.$$

The electrical conductivity therefore has its lowest value at about 100% H_2SO_4. When pure sulfuric acid is diluted with water, dissociation occurs increasingly, by the mechanism shown in the following equation:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-.$$

Conductivity increases accordingly. At between 92 and 84.5 wt% H_2SO_4, the monohydrate, $H_2SO_4 \cdot H_2O$, predominates in equilibrium with the ionic species, and conductivity therefore decreases slightly. At lower concentrations of H_2SO_4, the degree of both dissociation and conductivity increases. At high water contents, a second stage of dissociation becomes of increasing importance:

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}.$$

Because of the decreasing total concentration of sulfuric acid, however, conductivity reaches a maximum at about 30 wt% H_2SO_4 (the exact value depends on the temperature) and decreases steeply down to 0 wt% H_2SO_4. Diluted sulfuric acid is the preferred electrolyte for industrial metal electrowinning and electroplating because of its high conductivity and because of the chemical stability of the sulfate ion. To take advantage of maximal electrical conductivity, sulfuric acid of about 33 wt% is used in lead-acid (accumulator) batteries (Sander *et al.*, 1984).

The density (specific gravity) of sulfuric acid and of mixtures of sulfuric acid and sulfur trioxide (oleum) is dependent on the H_2SO_4 and SO_3 concentrations, the temperature and the pressure. At constant temperature, the density of sulfuric acid increases steeply with rising H_2SO_4 concentration, reaching a maximum at about 98%. From 98 to 100%, the density decreases slightly but rises again in the oleum range up to a concentration of about 60% free SO_3.

(*a*) *Description*: Clear, colourless, odourless, oily liquid (Budavari, 1989; Weast, 1989)

(*b*) *Boiling-point*: 330 °C; can vary over a range of 315–338 °C owing to loss of sulfur trioxide during heating to 300 °C or higher (Sax & Lewis, 1987; Weast, 1989)

(*c*) *Melting-point*: 10.36 °C (100%); 3.0 °C (98%); -32 °C (93%); -38 °C (78%); -44 °C (74%); -64 °C (65%) (Budavari, 1989; Weast, 1989)

(*d*) *Density*: See Table 1 for specific gravity at various acid strengths.
(*e*) *Solubility*: Miscible with water, with generation of much heat and with reduction in volume; decomposes in ethanol (Budavari, 1989; Weast, 1989)
(*f*) *Volatility*: Vapour pressure, 1 mm Hg (133 Pa) at 145.8 °C (Weast, 1989)
(*g*) *Stability*: Decomposes at 340 °C into sulfur trioxide and water (Budavari, 1989)
(*h*) *Reactivity*: Very corrosive; has great affinity for water, absorbing it from air and from many organic substances; dissolves most metals; concentrated acid oxidizes, dehydrates or sulfonates many organic compounds (Sax & Lewis, 1987; Budavari, 1989).
(*i*) *Conversion factor*: mg/m^3 = 4.0 × ppm[a]

3.2 Sulfur trioxide

Sulfur trioxide is the anhydride of sulfuric acid. It can exist as a gas, liquid or solid. In the gaseous and liquid phases, an equilibrium exists between the monomer, SO_3, and the cyclic trimer, S_3O_9. In the presence of slight traces of moisture (approximately 100 ppm H_2O), liquid sulfur trioxide (below about 27 °C) and solid sulfur trioxide are transformed to solid polymers, which form intergrown crystal needles. They consist of the α and β forms which are currently believed to correspond to long sulfur trioxide chains with water saturation at the chain ends. Pure, solid sulfur trioxide, referred to as γ-SO_3, forms silky orthorhombic (ice-like) crystals. The melting-points of the polymeric α and β forms given below indicate the temperatures at which these solid forms depolymerize to form liquid sulfur trioxide. Discrepancies in reported values for various physical properties of sulfur trioxide reflect, in part, the extreme sensitivity of these values to trace contamination with moisture (Sander *et al.*, 1984).

(*a*) *Description*: Colourless liquid that fumes in air, at room temperature and atmospheric pressure (Donovan & Salamone, 1983)
(*b*) *Boiling-point*: 44.8 °C (liquid) (Sander *et al.*, 1984)
(*c*) *Melting-point*: 62.3 °C (α), 32.5 °C (β), 16.8 °C (γ) (solid) (Donovan & Salamone, 1983)
(*d*) *Density*: 3.57 g/l at 0 °C (gaseous); 1.92 g/cm^3 at 20 °C (liquid); 2.29 g/cm^3 at −10 °C (γ, solid) (Donovan & Salamone, 1983; Sander *et al.*, 1984)
(*e*) *Volatility*: Vapour pressure (solid, at 25 °C), 73 mm Hg (10 kPa) (α), 344 mm Hg (46 kPa) (β), 433 mm Hg (58 kPa) (γ) (Budavari, 1989); liquid: 195 mm Hg (26 kPa) at 20 °C, 353 mm Hg (47 kPa) at 30 °C (Sander *et al.*, 1984); relative vapour density (air = 1), 2.003 (Anon., 1972)
(*f*) *Stability*: The α form appears to be the stable form (Sax & Lewis, 1987).
(*g*) *Reactivity*: Unreactive towards most metals in absolutely dry conditions; reacts with metal oxides at moderately high temperatures to form the respective metal sulfates; reacts instantaneously and violently with water to form sulfuric acid and with water vapour to form sulfuric acid mists; reacts readily with organic compounds, which may be sulfonated, oxidized or dehydrated (Sander *et al.*, 1984; Budavari, 1989).

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[a] Calculated from: mg/m^3 = (molecular weight/24.45) × ppm, assuming normal temperature (25 °C) and pressure (760 mm Hg [101.3 kPa])

(*h*) *Conversion factor*: mg/m^3 = 3.27 × ppm[a]

4. Technical products and impurities

Two commercial designations of acid strength are used for sulfuric acid: percentage sulfuric acid (% H_2SO_4) and degrees Baumé (°Bé) (Olin Chemicals, 1979). Degrees Baumé is defined as: °Bé = 145 – (145/specific gravity) (Sax & Lewis, 1987). For acid concentrations up to 93.2% H_2SO_4, the specific gravity of a solution is related to its concentration; at acid concentrations above that level, there is no consistent mathematical relationship, and these are referred to simply in terms of percentage sulfuric acid. The strength of oleum (fuming sulfuric acid) can be designated by the percentage of free dissolved sulfur trioxide or as the equivalent percentage of 100% H_2SO_4 (Olin Chemicals, 1979). Table 1 displays these relationships and the typical concentrations of sulfuric acid produced commercially, with some common uses.

Table 1. Acid strengths and end uses

H_2SO_4 (%)	°Bé	Oleum (% free SO_3)	Specific gravity	Uses
35.67	30.8	–	1.27	Storage batteries
62.18–69.65	50–55	–	–	Normal superphosphate and other fertilizers
77.67	60.0	–	1.7059	Normal superphosphate and other fertilizers; isopropyl and *sec*-butyl alcohol production
80.00	61.3	–	1.7323	Copper leaching
93.19	66.0	–	1.8354	Phosphoric acid, titanium dioxide production
98.99	–	–	–	Alkylation, phosphoric acid, boric acid production
104.50[a]	–	20	1.9056	
106.75[a]	–	30	1.9412	
109.00[a]	–	40	1.9737	Caprolactam, nitrations and sulfonations, dehydration, blending with weaker acids
111.25[a]	–	50	1.9900	
113.50[a]	–	60	1.9919	
114.63[a]	–	65	1.9842	

From West & Smith (1983); Sander *et al.* (1984)
[a]Percentage equivalent H_2SO_4

Originally, sulfuric acid was marketed in four grades, known as chamber acid, 50 °Bé; tower acid, 60 °Bé; oil of vitriol, 66 °Bé; and fuming acid. Today, sulfuric acids are commonly specified as commercial, electrolyte (high purity for batteries), textile (low organic content) and chemically pure or reagent grades (West & Smith, 1983; US Environmental Protection Agency, 1985). Sulfuric acid is produced in grades of exacting purity for use in storage batteries and for the rayon, dye and pharmaceutical industries and to less exacting

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[a]Calculated from: mg/m^3 = (molecular weight/24.45) × ppm, assuming normal temperature (25°C) and pressure (760 mm Hg [101.3 kPa])

specifications for use in the steel, heavy chemical and fertilizer industries (West & Duecker, 1974).

The range of specifications of impurities in several grades and concentrations are (ppm, max.): ammonium, 10; antimony, 0.03–1.0; arsenic (see IARC, 1987), 0.3–50.0; bismuth, 0.1; cadmium (see IARC, 1987), 0.05–1.0; chlorides, 0.5–10; copper, 0.2–50; iron, 25–200; lead (see IARC, 1987), < 1.0–4.0; manganese, 0.2–0.3; mercury, 1; nickel (see IARC, 1990), 0.3–1.0; nitrates, 5–150; selenium (see IARC, 1975), 0.1–20; sulfurous acid (as SO_2), 40; and zinc, 0.3–40 (American Smelting and Refining Co., 1988; Du Pont Co., 1988; Akzo Chemicals, undated; Boliden Intertrade, undated; Koch Sulfur Products, undated a,b).

In many processes in which sulfuric acid is used, waste or 'spent' sulfuric acid must be disposed of. In some cases, the spent acid is returned to the manufacturer, who then reprocesses it for captive consumption or resale (see also pp. 48–49). Spent sulfuric acid is available at a purity range of 70.0–75.0% with the following allowable impurities (ppm, max.): free chlorine, 500; iron, 100; organics, 50; fluorides, 10; calcium, 5; sodium, 10; mercury, 0.15; lead, 50; and chloride, 100 (Occidental Chemical Corp., 1983).

Oleum is available in several grades (free SO_3 ranging from 20 to 99.9% and the corresponding percentage H_2SO_4 equivalents ranging from 104.5 to 122.5%), with the following specifications for impurities (ppm, max.): arsenic, 0.05; chlorides, < 1; iron, 1–40; and lead, < 1 (Du Pont Co., 1987, 1988; Boliden Intertrade, undated).

Sulfur trioxide is available as technical-grade stabilized (with a proprietary stabilizer) and unstabilized liquids with a minimal purity of 99.5%, a maximal sulfuric acid content of 0.4% and a maximal iron content of 5.0 ppm (Du Pont Co., 1980).

5. Analysis

Selected methods for the analysis of sulfuric acid in air and stack gases are presented in Table 2.

6. Use

Sulfuric acid is one of the most widely used of all industrial chemicals. Most of its uses may be considered indirect, because it is used as a reagent rather than an ingredient; little of it appears in end products and most finishes as spent acid or some kind of sulfate waste. A number of products contain sulfur derived from sulfuric acid, but nearly all of them are low-volume, specialty products (Sander *et al.*, 1984).

The principal use of sulfuric acid is in the manufacture of fertilizers (both phosphate and ammonium sulfate types). Other significant applications include rayon and other fibres, pigments and colours, explosives, plastics, coal-tar products such as dyes and drugs, storage batteries, synthetic detergents, natural and synthetic rubber, pulp and paper, cellophane and catalysts. It is also used to make inorganic chemicals such as hydrochloric acid, hydrofluoric acid, aluminium sulfate, copper sulfate and chromium chemicals. It is used in petroleum refining, in pickling iron, steel and other metals and in ore concentration (Sander *et al.*, 1984; Mannsville Chemical Products, 1985).

Table 2. Methods for the analysis of sulfuric acid

Sample matrix	Sample preparation	Assay procedure	Limit of detection	Reference
Air	Pass through heater (120°C); then through a diffusion denuder; then through detector	FPD	1-2 $\mu g/m^3$	Appel *et al.* (1987)
	Draw through silica gel tube; desorb with sodium bicarbonate/-sodium carbonate and heat	IC	4 µg/sample (~0.5 mg/m^3)	Eller (1984)
	Collect on cellulose filter paper; heat for 72 h; compare charring coloration to standard	Colorimetric	15 µg (~0.2 mg/m^3)	Taylor (1979)
	Absorb in water in midget impinger; precipitate as barium sulfate; measure turbidity at 420 nm	Turbidimetry	10 µg (0.1 mg/m^3)	Taylor (1977a)
	Collect on cellulose membrane; extract with distilled water and isopropanol; titrate using 0.005 M barium perchlorate and Thorin indicator	Titration	0.5 mg/m^3 (lower validated value)	Taylor (1977b)
Stack gases	Collect *via* impinger (using controlled condensation method); titrate using sodium hydroxide and bromophenol blue indicator	AT	40 mg/m^3	Knapp *et al.* (1987)
	Extract isokinetically; separate sulfuric acid mist (including sulfur trioxide) and sulfur dioxide; add isopropanol; titrate using 0.01 M barium perchlorate and Thorin indicator	Titration	NR 0.05 mg/m^3 (SO_3) 1.2 mg/m^3 (SO_2)	US Environmental Protection Agency (1989)
Water, wastes	Add solid barium chloranilate; measure colour intensity	Colorimetric	NR 10-400 mg/l	US Environmental Protection Agency (1986a)
	Pass through a sodium-form cation-exchange column; react with ethanol solution of barium chloride and methylthymol blue at pH 2.5-3.0; raise to pH 12.5-13.0; measure colour intensity	Colorimetric	NR 0.5-300 mg/l	US Environmental Protection Agency (1986b)
	Convert sulfate ion to a barium sulfate suspension; compare turbidity to a standard curve	Turbidimetry	1 mg/l	US Environmental Protection Agency (1986c)

Abbreviations: AT, alkalimetric titration; FPD, flame photometric detection; IC, ion chromatography; NR, not reported

In the production of fertilizers, sulfuric acid is used to digest phosphate rock (chiefly calcium phosphate) to produce superphosphate. In the manufacture of phosphoric acid, calcium sulfate (gypsum) is a by-product. Ammonium sulfate fertilizers are made directly from ammonia, as a by-product of caprolactam manufacture or by recovery from coke oven gases. Substantial quantities of sulfuric acid are used as a medium for acidic dehydrating reactions in organic chemical and petrochemical processes involving reactions such as nitration, condensation and dehydration. In the petroleum industry, sulfuric acid is used as an alkylation catalyst and in the refining of lubricating oil; recently, it has been replaced by hydrofluoric acid in this use. Sulfuric acid is also used extensively in the manufacture of catalytic cracking catalysts. In the steel industry, it is used in 'pickling', in which steel is freed of the oxide coating that forms during heating for casting, forging, rolling or annealing. Pickling is used in the surface treatment of other metals, including cadmium, chromium, copper, gold, nickel, silver, tin and zinc. Sulfuric acid is also used in other processes requiring the acid treatment of metals, such as electroplating and etching (Sander *et al.*, 1984; Mannsville Chemical Products, 1985). (See the monograph on occupational exposure to mists and vapours from sulfuric acid and other strong inorganic acids for details of some of these processes.)

Under certain conditions, sulfuric acid is used directly in agriculture for rehabilitating extremely alkaline soils; this is, however, not a widespread use. Probably the largest use of sulfuric acid in which its sulfur becomes incorporated in the final product is organic sulfonation, particularly for the production of detergents. Other, minor organic chemicals and pharmaceuticals are made by sulfonation. One of the most familiar consumer products that contains sulfuric acid, the lead–acid (accumulator) battery, accounts for only a tiny fraction of total sulfuric acid consumption (Sander *et al.*, 1984).

In the production of fibres such as viscose rayon, the viscous alkaline solution is run through spinnerettes and forms filaments which are coagulated as they pass through a sulfuric acid spinning bath. In the sulfate process for producing titanium dioxide, sulfuric acid is used to digest titanium ore; however, this use is declining because of environmental problems and the greater efficiency of the chloride process. Other uses for sulfuric acid include pharmaceuticals, pesticides, dyes and electronic etchants. Fuming sulfuric acid (oleum) is used as the sulfonating agent in synthetic detergents (Mannsville Chemical Products, 1985).

Sulfur trioxide is used primarily as a sulfating or sulfonating agent. The reactivity of sulfur trioxide eliminates the need for excess sulfonating agent, so neutralization of excess sulfonating agent is not required, and salt-free products can be produced. Unlike sulfuric acid and some other sulfonating agents, sulfur trioxide is miscible in a number of solvents, such as liquid sulfur dioxide and various halogenated organic solvents. Pyridine, dioxane, trimethylamine, dimethylformamide and other Lewis bases are used as complexing agents and moderate the reactivity of sulfur trioxide. Vaporized sulfur trioxide, diluted with dry air or nitrogen, is often used in place of liquid sulfur trioxide (Du Pont Co., 1980).

In the detergent industry, sulfur trioxide sulfonation is used to produce alkyl–aryl sulfonates, and particularly dodecylbenzene sulfonate. Alkylated benzene produced from straight-chain, normal paraffins may be sulfonated with sulfur trioxide to produce linear alkylated sulfonates. These materials are widely used in industrial detergents and are highly biodegradable under aerobic conditions. Sulfation of long-chain primary alcohols, such as lauryl alcohol, produces alkylsulfates, which are used in detergent powders, in dishwashing formulations and as shampoo ingredients. These products are biodegradable, as are the ethoxylated alcohol sulfates produced from ethoxylated alcohols and sulfur trioxide. Fats and oils such as castor, lard, soya bean and peanut, may be sulfonated with sulfur trioxide to produce wetting agents, detergents and emulsifiers (Du Pont Co., 1980).

In the chemical industry, sulfur trioxide is used to prepare linear, water-soluble, sulfonated polystyrenes which are used as ion-exchange resins and dispersing agents. Sulfur trioxide is also incorporated to sulfonate benzene in the preparation of benzene sulfonic acid, which is used in the manufacture of phenol by the alkali fusion method (Du Pont Co., 1980).

Substituted benzenes sulfonated with sulfur trioxide are involved in the synthesis of a number of intermediates for dyestuffs, drugs and insecticides. Sulfur trioxide is used to convert long-chain alkylated benzenes to oil-soluble sulfonates for lubricant additives, emulsifiers and rust preventives. Addition of low levels of sulfur trioxide to off-gases improves the efficiency of electrostatic fume precipitators. Surface sulfonating of a number of polymers with sulfur trioxide increases their resistance to permeation by gases and hydrocarbons (Du Pont Co., 1980).

The annual estimated patterns of use of sulfuric acid in the USA over several years are presented in Table 3. Patterns of use may vary from country to country. For example, whereas in most countries 60–70% of the sulfuric acid is used in the manufacture of fertilizers, in Germany in 1978 the fertilizer industry accounted for only about 14% of sulfuric acid consumption, owing to the historical predominance of other processes (Sander *et al.*, 1984; Zengtai, 1984).

Table 3. Annual estimated patterns of use (%) of sulfuric acid in the USA

Use	1970	1978	1983	1984	1985	1987	1988
Phosphate fertilizers	54	67	72	70	70	67	68
Petroleum refining	8	5	7	5	5	8	7
Mining and metallurgy	6	6	–	5	–	4	–
Inorganic chemicals and pigments	6	4	4	4	4	4	4
Ore processing (mostly copper leaching)	1	2	2	–	3	–	3.5
Industrial organic chemicals	6	4	3	3	2.5	4	3.5
Synthetic rubber and plastics	–	–	3	3	2.5	2	2.5
Pulp and paper	–	–	2	2	2	2	2.5
Soap and detergents	–	–	–	1	–	1	–
Water treatment chemicals	–	–	1	1	–	1	–
Cellulose fibres and films (including rayon and cellophane)	2	1	–	1	–	1	–
Inorganic pigments and paints	6	2	1	–	–	–	–
Other	11	9	5	5	11	6	9

From West & Smith (1983); Anon. (1985); Mannsville Chemical Products (1985); US Environmental Protection Agency (1985); Mannsville Chemical Products (1987); Anon. (1988)

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