

SULPHURIC ACID

E.U. Classification:

C: corrosive



UN N°: 1830

MARPOL classification: C until 31/12/2006

Y from 01/01/2007

SEBC Classification: D (dissolver)



SULPHURIC ACID

PRACTICAL GUIDE

INFORMATION

DECISION-MAKING

RESPONSE

This document was drafted by *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) with financial support from ARKEMA and the French Navy, as well as technical guidance from ARKEMA.

Caution

Certain data, regulations, values and norms may be liable to change subsequent to publication. We recommend that you check them.

The information contained within this guide is a result of *Cedre's* research and experience. *Cedre* cannot be held responsible for the consequences resulting from the use of this information.

Published: November 2006
Legal deposit upon publication

Translated by Sally Ferguson

Purpose of this guide

As part of the research funded by the French Navy and ARKEMA, *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) has produced a series of response guides for chemical hazards. They can be used to assist in emergency response in the event of an incident involving a vessel carrying hazardous substances which may cause water pollution.

These guides are updates of the 61 "mini response guides" published by *Cedre* in the early 1990s.

These guides are designed to allow rapid access to the necessary initial information (see chapter entitled "First line emergency data"), in addition to providing relevant bibliographical sources to obtain further information.

They also contain the results of scenarios relating to incidents which have occurred in the Channel, the Mediterranean and in rivers. These scenarios are only intended to provide response authorities with indications of what to do in an emergency. Each real incident should be analysed individually and the response authorities should not underestimate the importance of taking in-situ measurements (air, water, sediment and marine fauna) in order to determine exclusion areas.

These guides are intended primarily for specialists who know about the techniques to use in the event of an emergency in addition to the relevant operational response measures. The main concern is to mitigate the consequences of a spill, however we cannot afford to overlook responder safety and human toxicology.

To contact the duty engineer at *Cedre* (24/7)
Please call: + 33 (0)2 98 33 10 10

National toxicology surveillance system in the event of a major toxicological threat.

In France, a hotline is manned around the clock by Division 7 of the General Department of Health (SD7/DGS).

During opening hours please call:
Tel.: + 33 (0)1 40 56 47 95
Fax: + 33 (0)1 40 56 50 56

Outside normal working hours please call the relevant authority.

Poison Control Centres in France

Angers (Centre Hospitalier d'Angers) Tel.: + 33 (0)2 41 48 21 21
Bordeaux (Hôpital Pellegrin-Tripode) Tel.: + 33 (0)5 56 96 40 80
Grenoble (Hôpital Albert Michallon) Tel.: + 33 (0)4 76 76 56 46
Lille (Centre Hospitalier Universitaire) Tel.: + 33 (0)8 25 81 28 22
Lyon (Hôpital Edouard Herriot) Tel.: + 33 (0)4 72 11 69 11
Marseille (Hôpital Salvator) Tel.: + 33 (0)4 91 75 25 25
Nancy (Hôpital Central) Tel.: + 33 (0)3 83 32 36 36
Paris (Hôpital Fernand Widal) Tel.: + 33 (0)1 40 05 48 48
Reims (Hôpital Maison Blanche) Tel.: + 33 (0)3 26 78 48 21
Rennes (Hôpital de Pontchaillou) Tel.: + 33 (0)2 99 59 22 22
Rouen (Hôpital Charles Nicolle) Tel.: + 33 (0)2 35 88 44 00
Strasbourg (Hôpitaux Universitaires) Tel.: + 33 (0)3 88 37 37 37
Toulouse (Hôpital de Purpan) Tel.: + 33 (0)5 61 77 74 47

Contents

Purpose of this guide	4
A WHAT YOU NEED TO KNOW ABOUT SULPHURIC ACID	6
B FIRST LINE EMERGENCY DATA	7
B.1 - First aid information	8
B.2 - ID card	9
B.3 - Physical data	10
B.4 - Flammability data	11
B.5 - Toxicological data	12
B.6 - Ecotoxicological data	13
B.7 - Persistence in the environment	14
B.8 - Classification	15
B.9 - Particular risks	17
B.10 - Transportation, handling, storage	18
C RESULTS OF ACCIDENT SCENARIOS	19
C.1 - Reminder of chemical properties	20
C.2 - Accident scenarios	21
C.3 - Consumption scenarios	32
D RESPONSE	33
D.1 - Experience feedback	34
D.2 - Examples of sulphuric acid spills	36
D.3 - Response recommendations	37
D.4 - Response techniques	39
D.5 - Choosing personal protective equipment (PPE)	40
D.6 - Measuring equipment and waste treatment	42
E FURTHER INFORMATION	43
E.1 - Glossary	44
E.2 - Acronyms	48
E.3 - Useful websites	50
E.4 - Bibliography	51
Annexes	53
Annex 1: pH graphs	54
Annex 2: summary and additional physical and toxicological data	56
Annex 3: fax format data card	60
Annex 4: classification of noxious liquid substances	63
Annex 4b: new classification of noxious liquid substances	64

What you need to know about sulphuric acid

A

Definition

Concentrated sulphuric acid is a colourless, odourless liquid. In air at room temperature, the concentrated acid gives off invisible toxic vapours. From 30°C, it gives off heavy, whitish, irritating vapours. The presence of impurities often turns the acid a yellowy brown colour.

Manufactured sulphuric acid exists as an aqueous solution at various concentrations. The data provided in this guide applies to sulphuric acid at concentrations of 92% to 98%.

Use

Sulphuric acid is used in the manufacture of fertilisers (superphosphates), the synthetic textile industry, the iron and steelmaking industry to remove oxidation, rust and scale, in ore processing, the oil industry, the manufacture of dyes, for electroplating, in the explosive industry, in the paper industry, as a dehydrating and sulphonating agent, and in lead batteries. It is a liquid chemical which is transported in bulk.

Risks

- Explosion: sulphuric acid is not an explosive compound, however it reacts violently with many organic matters, powdered metals, carbides, chlorates, chromates, permanganates, nitrates, fulminates and fluosilicon, to produce a lot of heat and releasing hydrogen. A dangerous, violent reaction occurs when concentrated sulphuric acid comes into contact with water. The reaction also causes projections of water to be sprayed. Concentrated sulphuric acid reacts violently with strong anhydrous bases or concentrated alkaline solutions.

- Fire: sulphuric acid is a flammable compound, however its corrosive action on most common metals (zinc, iron, some cast irons and copper) is accompanied by a release of hydrogen, an explosive and flammable gas when mixed with air. **Warning: the minimum ignition energy of hydrogen is very low.**

- Toxicity: sulphuric acid is liable to be absorbed by the respiratory and digestive tracts, after a violent reaction with water. In solution or in the form of vapours, it is corrosive and irritating for the skin, eyes and the respiratory and digestive tracts. The risks for man and for the environment are therefore mainly due to the corrosive nature of sulphuric acid when in contact with this chemical. Repeated or prolonged contact with the skin can cause dermatitis.

Behaviour in the environment

When spilt into water, sulphuric acid is a strong acid which completely dissolves into sulphate ions and protons, **causing the release of a lot of heat**. If this mixture occurs on or just below the water surface, the water can be brought to the boil. However, given its high density ($d = 1.84$), the acid sinks if there is no agitation.

Its toxicity depends above all on the acidity of the substance and its effect on the pH: it is noxious for certain aquatic species whose survival requires a pH of at least 5.5. It presents no danger of bioconcentration or bioamplification along the food chain.

There is however a danger for the water quality if large quantities infiltrate the ground and/or natural waters.

First line emergency data

- First aid information _____ **B1**
- ID card _____ **B2**
- Physical data _____ **B3**
- Flammability data _____ **B4**
- Toxicological data _____ **B5**
- Ecotoxicological data _____ **B6**
- Persistence in the environment _____ **B7**
- Classification _____ **B8**
- Particular risks _____ **B9**
- Transportation, handling, storage _____ **B10**



First aid information (ICSC, 2000; ARKEMA MSDS, 2003)

The corrosive action of sulphuric acid can appear after a certain delay: it is important to take immediate action.

Immediately remove all soiled or spotted clothes, including shoes.

Intoxication by inhalation

- Move the victim into the open air and lie them down.
- Prop the person up to a half-sitting position.
- Apply artificial respiration if necessary.
- Transfer to hospital immediately.

B1

Skin contact

- Rinse with plenty of water at length while rapidly removing soiled clothes in the shower.
- Finish cleaning with a neutralising solution (5 to 10 % triethanolamine solution).
- In the event of extensive burns, transfer to hospital immediately.

Eye contact

- Immediately wash the eyes with plenty water for at least 15 minutes, keeping the eyelids open.
- Consult a specialist.

Intoxication by ingestion

- Do not induce vomiting.
- Rinse the mouth and lips with water if the person is conscious.
- Transfer to hospital immediately.

Where necessary, contact the nearest poison control centre (cf. page 4).

ID card¹

Sulphuric acid

Gross formula: H_2SO_4
Semi-developed formula: $(\text{OH})_2-\text{S}=\text{O}_2$

Synonyms

Sulfuric acid, oil of vitriol, vitriol, battery acid, chamber acid, fertilizer acid, mattling acid, electrolyte acid, dihydrogen sulphate.

B2

E.U. Classification

C: corrosive

R35: causes severe burns.

S26: in case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S30: never add water to this product.

S45: in case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

CAS n°:	7664-93-9
EC N° (EINECS):	231-639-5
Index n°:	016-020-00-8

Classification for transportation

UN N°:	1830
Class:	8

¹ Additional data and sources in annex 2

Physical data*

Conversion factor (air: 20° C):

$$1 \text{ ppm} = 4.38 \text{ mg/m}^3$$

$$1 \text{ mg/m}^3 = 0.25 \text{ ppm}$$

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

B3

Molar mass	98.08 g/mol (INRS, 1997)
Boiling point at 1 atm	335°C (98 %) (ARKEMA MSDS, 2003) 290°C (92 %) (GRANDE PAROISSE MSDS, 2003)
Freezing point	-15°C (94 to 96 %) (ARKEMA MSDS, 2003) -10°C / +5°C (97 %) (ARKEMA MSDS, 2003) +5°C (98 %) (ARKEMA MSDS, 2003)
Critical temperature	N/A
Relative density (water = 1)	1.84 at 20°C (93 to 100 %) (SIDS OCDE, 2001)
Vapour density (air = 1)	3.4 (ICSC, 2000)
Solubility in fresh water	soluble in water at 20°C (ARKEMA MSDS, 2003) (with heat production)
Vapour pressure/tension	< 0.001 hPa at 20°C (DIPPR, 2005)
pH of the solution	very acidic < 1 (94 to 98 %) (ARKEMA MSDS, 2003; GRANDE PAROISSE MSDS, 2003)
pK _a	1 st pK _a value < 0 2 nd pK _a value = 1.92 (SIDS OCDE, 2001)
Viscosity at 25°C	21 mPa.s (ENVIRONMENT CANADA ENVIROGUIDE, 1984)
Olfactory threshold in air	> 0.25 ppm (1 mg/m ³) (ENVIRONMENT CANADA ENVIROGUIDE, 1984)

Definitions in glossary

*For certain data entries, the acid concentration is specified in brackets.

Flammability data

(ARKEMA MSDS, 2003)

Explosive limits

Non-flammable product

Flash point

Non-flammable product

Self-ignition point

Non-flammable product

Dangerous products of decomposition

Formation of flammable hydrogen by corrosion of metals

Breakdown by fire into sulphur oxides (sulphur trioxides and dioxides), which are toxic gases.

Behaviour when in contact with other products

Sulphuric acid is non-flammable, however it causes:

- violent reactions with a risk of explosion with many organic matters, powdered metals (zinc, iron, certain cast irons, copper), carbides, chlorates, chromates, permanganates, nitrates, fulminates and fluosilicon
- a violent and dangerous reaction if water is added to concentrated sulphuric acid causing spray
- a violent reaction with strong anhydrous bases or concentrated alkaline solutions.

B4

Toxicological data

(ARKEMA MSDS, 2003; CSST, 2000)

Sulphuric acid is a corrosive substance for the skin and mucous membranes upon contact; the intensity and nature of the lesions caused will depend on the concentration of the acid and the duration of exposure.

Acute human toxicity

- By ingestion: burns to the mouth and digestive tract with laryngeal oedema, vomiting of blood, possible perforation of digestive tract and a state of shock.
- By skin contact: severe burns.
- By eye contact: redness, pain, oedema, corneal opaqueness and possible loss of sight.

If concentrated solutions of sulphuric acid come into contact with the skin or eyes, they cause local caustic lesions if the affected area is not rapidly decontaminated.

- By inhalation: exposure to vapours causes coughing, breathing difficulties and can lead to bronchial irritation and pulmonary oedema in the presence of high concentrations. The effects are influenced by several factors including the particle size, the concentration of the product and the degree of humidity. Physical exercise can exacerbate symptoms.

Asthmatics are more sensitive to the bronchoconstrictor effects of inhaled acid.

Chronic human toxicity

- Repeated exposure by inhalation: dental erosion and chronic bronchitis.
- Irritant contact dermatitis can arise in the case of repeated contact with sulphuric acid or its solutions.
- The ACGIH (notation A2) and IARC (group 1) believe that exposure to mists of strong inorganic acid containing sulphuric acid is carcinogenic for humans.

Threshold toxicological values

Occupational exposure values

MEV (France): 0.25 ppm (1 mg/m³)

ELV (France): 0.75 ppm (3 mg/m³)

TLV-TWA (ACGIH): 0.05 ppm (0.2 mg/m³)

Risk management values for the population

IDLH (NIOSH): 3.75 ppm (15 mg/m³)

TLV-STEL (ACGIH): data unavailable

TEEL 0: 0.25 ppm (1 mg/m³)

ERPG 1: 0.50 ppm (2 mg/m³)

ERPG 2: 2.50 ppm (10 mg/m³)

ERPG 3: 7.50 ppm (30 mg/m³)

Specific effects

Carcinogenic effects: a review of epidemiological studies tends to show a certain association between exposure to mists of strong inorganic acids containing sulphuric acid and the presence of cancer of the respiratory tract, and in particular laryngeal cancer and lung cancer (SIDS OCDE, 2001).

Effects on fertility: no data available.

Teratogenic effects and/or effects on foetal development: not demonstrated.

Mutagenic effects: not demonstrated.

Ecotoxicological data

(ARKEMA MSDS, 2003; SIDS OCDE, 2001)

Acute ecotoxicity

Crustacean (<i>Daphnia magna</i>)	EC ₅₀ (24h) = 29 mg/L (fresh water)
Fish (<i>Brachydanio rerio</i>)	LC ₅₀ (24h) = 82 mg/L (fresh water)
Fish (<i>Lepomis macrochirus</i>)	LC ₅₀ (48h) = 49 mg/L (fresh water)
Fish (<i>Pleuronectes platessa</i>)	LC ₅₀ (48h) = 100 to 330 mg/L (seawater)

Chronic ecotoxicity

Seaweed (<i>Gymnodium sp.</i>)	NOEC at pH 5.6 = 0.13 mg/L
Insect (<i>Tanytarsus dissimilis</i>)	NOEC (35 d) = 0.15 mg/L (fresh water)
Fish (<i>Jordanella floridae</i>)	NOEC = 0.025 mg/L (fresh water)
Fish (<i>Savelinus fontinalis</i>)	NOEC embryonic survival = 0.31 mg/L at pH 5.2 (fresh water) NOEC embryonic survival = 0.15 mg/L at pH 5.5 (fresh water) NOEC weight at 10 months = 0.13 mg/L at pH 5.5 (fresh water)
Mesocosm studies:	
Fish (<i>Savelinus fontinalis</i>)	NOEC = 0.13 mg/L at pH 5.56 (fresh water)
Phytoplankton	NOEC = 0.13 mg/L at pH 5.6 (fresh water)
Lake-dwelling fish	NOEC = 0.0058 mg/L at pH 5.93 (fresh water)

PNEC (Predicted No-Effect Concentration): no PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a sulphuric acid spill, the change in pH of the water must be calculated or measured. **Variation by one pH unit could affect flora and fauna.** The average pH of water can vary in seawater from 8 to 8.4 (stable pH with high buffering capacity) and in fresh water from 6 to 7.5.

Examples of pH in natural waters

Brest's estuary	Fos sur Mer	Fresh water
8	7.95	6 - 7.5

Definitions in glossary

Persistence in the environment

The risk presented by sulphuric acid for the environment is due to hydronium ions (pH effect). The effect of sulphuric acid therefore depends on the buffering capacity of the aquatic or terrestrial ecosystem. A pH of less than 5.5 is harmful for aquatic life. The effect of this ion is naturally reduced by dilution and in seawater by a buffering effect.

Risk for the environment

A high concentration of sulphuric acid in the water will increase the acidity of the water, which can be harmful for aquatic life.

In seawater, some types of algae can survive at a pH of 6, but cannot endure a decrease in pH to less than 5.5.

Fresh water fish cannot survive at a pH of less than 4.5. Marine organisms generally cannot endure significant variations in pH (cf. graph below).

Breakdown

Sulphuric acid reacts rapidly with the ions present in the environment and transforms into salts.

Bioaccumulation

Sulphuric acid is an inorganic substance which does not bioaccumulate along the food chain.

Indirect pollution

Sulphuric acid is a strong acid which can lead to the release of the metal ions contained in the mud or sediments present at the base of the water column (case for lakes and ports).

B7








Partition coefficient for organic carbon and water (Koc): N/A

Partition coefficient for octanol and water (Kow): N/A

Bioconcentration factor (BCF): N/A

Degrees of acidity tolerated by the fresh water environment

(Diagram produced based on the Atmosphere, Climate & Environment Information Programme)

pH	7.5	7	6.5	6	5.5	5	4.5	4
			crustaceans, molluscs					
			salmon, roach					
			sensitive insects & plant and animal plankton					
			rainbow trout, greyling					
			perch, pike					
			eels, brook trout					
			water lilies, reeds					

Classification

IBC Code (IMO, 2004):

- hazards: S/P (safety/pollution risk)
- ship type: 3
- tank type: 2G (integral gravity tank)
- tank vents: open
- tank environment: no
- electrical equipment:
class I'': NF (non-flammable)
- gauging: O (open type)
- vapour detection: no
- fire protection: no
- materials of construction: no particular instruction

B8

SEBC Classification: D (dissolver)

MARPOL classification: C (definition in annex 4) until 31/12/2006
Y (definition in annex 4b) from 01/01/2007

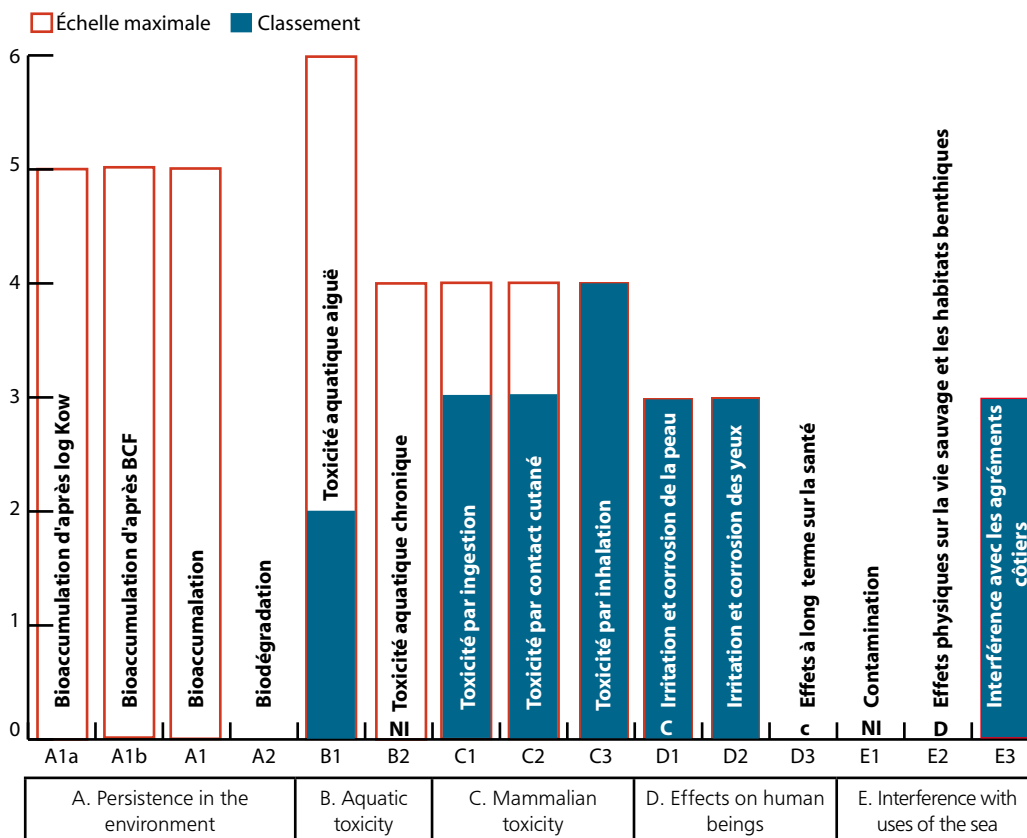
E.U. Classification:



C: corrosive

R35	Causes severe burns.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S30	Never add water to this product.
S45	In case of accident or if you feel unwell, seek medical advice. Show the label where possible.
231-639-5	E.C. N° (EINECS)

GESAMP Classification of sulphuric acid (GESAMP, 2006)



A1a, A1b: sulphuric acid is an inorganic substance

A1: inorganic, non-bioaccumulable product

A2: inorganic product

B1: slight acute aquatic toxicity

B2: NI: No Information

C1: relatively high toxicity when ingested by mammals

C2: relatively high toxicity by skin contact with mammals

C3: relatively high toxicity through inhalation by mammals

D1: C: Corrosive substance. Complete necrosis of the skin < 3 minutes

D2: severely irritating for eyes leading to irreversible corneal lesions

D3: carcinogenic

E1: NI: No Information

E2: D: Dissolves

E3: highly objectionable, closure of amenity.

Particular risks

Danger (CEFIC ERICARD, 2003)

- Heating the receptacle can cause an increase in pressure and the receptacle may shatter.
- In the presence of heat, sulphuric acid breaks down into sulphur oxides and water.
- Possibility of attacking metals, in the presence of heat or humidity, and production of hydrogen which may form an explosive mixture with air.

Vapours are invisible and heavier than air. They spread out across the ground and can infiltrate drains and underground systems.

Stability and reactivity (ARKEMA MSDS, 2003)

- Keep away from heat.
- Substances to be avoided: metals (in the presence of heat or humidity), propargyl alcohol (explosive reaction), water, bases (exothermic reaction), combustible matters (carbonisation) and oxidants.
- Hygroscopic substance: it absorbs water from damp air.
- Dangerous products of decomposition: formation of flammable hydrogen by corrosion of metals.

B9

Behaviour when in contact with other products (ENVIRONMENT CANADA ENVIROGUIDE, 1984)	
Organic acids	Production of heat and formation of toxic vapours
Hydrochloric acid, ammonia water	Production of heat, increase in pressure in closed containers
Alcohols, glycols, amides and amines	Production of heat and formation of toxic vapours
Copper	Formation of toxic vapours (SO ₂)
Polymerisable compounds	Sudden polymerisation and production of heat and toxic vapours
Aromatic hydrocarbons	Heat, fire
Alkaline metals and alkaline earth metals	Violent reaction, fire, explosion, formation of flammable gases
Nitrobenzene	Explosion, formation of flammable gas (H ₂)
Hydrogen peroxide	Violent explosion

Transportation, handling, storage

Transportation (ARKEMA MSDS, 2003)

Identification n° (UN): 1830

Land transportation:

RID (rail) /ADR (road)

Hazard classification: 80

Class: 8

Packaging group: II

Classification code: C1

Labels: 8

Transportation via inland waterways:

ADN/ADNR

Hazard classification: 80

Class: 8

Classification code: C1

Labels: 8

Maritime transport: IMDG

Class: 8

Packaging group: II

Marine pollutant: No

Labels: 8

Air freight: IATA

Class: 8

Packaging group: II

Labels: 8

Handling (ARKEMA MSDS, 2003)

In high concentration of vapours:

- Ventilate and evacuate appropriately.
- Provide showers and eye washers.
- Ensure that there is a water source nearby.
- Ensure that SCBA (Self-Contained Breathing Equipment) is available nearby.

Use

- Eliminate all sources of ignition at tank openings. No smoking.
- Hot works permit for cutting and welding operations.
- Do not add water to the acid.
- Gradually put the acid into contact with the water (strong exothermic reaction).
- Immediately remove pools of the product.

Storage

- Prevent all arrivals of water.
- Keep away from heat.
- Store outdoors.
- Store in firmly closed receptacles in a cool and well aerated place.
- Store in tanks equipped with dehydrating breathers.
- Provide a retention tank and ensure that the ground is impermeable and resistant to corrosion, with a drainage system sending run-off to a neutralisation tank.
- Ground the tanks and ensure that the electric equipment is watertight.

Incompatible products

- Propargyl alcohol (explosive reaction).
- Water, bases, combustible substances, oxidants.

Recommended packaging materials

- For small quantities: ordinary steel.
- For large quantities: stainless steel (NSMC or NS 22S), carbon steel.
- Packaging materials to be avoided: light metals and alloys in the presence of humidity, including for parts in contact with the product.

Results of accident scenarios

- Reminder of properties ————— C1
- Accident scenarios ————— C2
- Consumption scenarios ————— C3

C

Reminder of properties

Transportation

Sulphuric acid is transported in liquid form in stainless steel tanks.

Vapour density and tension

- Relative density: 1.84 at 20°C
- Vapour density: 3.4
- Vapour tension: < 0.001 hPa at 20°C

Solubility

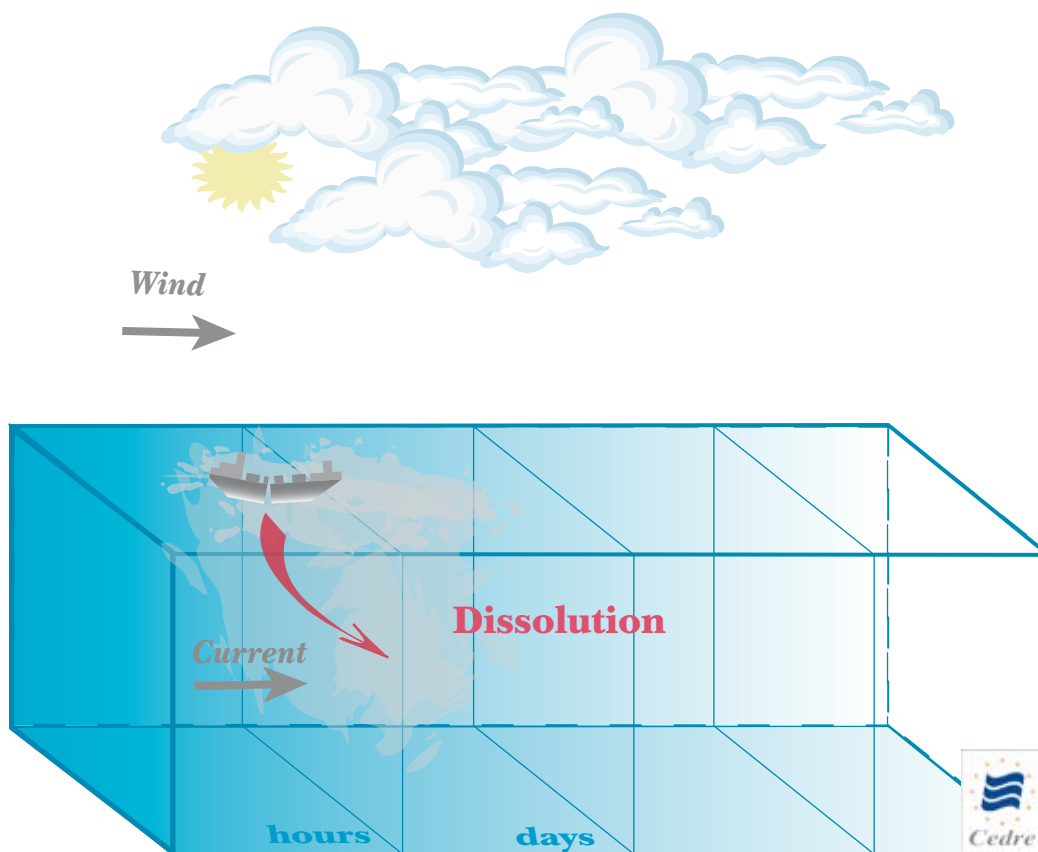
Sulphuric acid is completely soluble in water.

Behaviour in the environment

Sulphuric acid is a strong acid which completely dissolves into sulphate ions and protons when spilt into water, causing the release of a lot of heat. If this mixture occurs just below the water surface, the water can be brought to the boil. However, given its high density ($d = 1.84$), the acid is likely to sink if there is no agitation.

In high concentrations, it leads to a significant decrease in pH, and therefore an acidification of the environment, harmful for aquatic life. In the atmosphere, there is no release of a gas cloud, except in the area immediately surrounding the leak where acid vapours can be produced.

C1



Behaviour of sulphuric acid spilt at sea

Accident scenarios

The scenarios defined here are simply designed to give an indication of the possible behaviour of sulphuric acid. In the event of a real spill, the results of simulations will naturally be different from those given here. The CHEMMAP behaviour model, the emergency response model employed by *Cedre*, was used for these simulations. Other more sophisticated models exist, but require response times which are incompatible with an emergency situation.

Four sulphuric acid spill scenarios are given here with different quantities of spilt acid:

- a high sea scenario (Channel): 10 kg/h, 1000 kg/h and 100 t/h of sulphuric acid spilt over 5 hours and 500 tonnes of sulphuric acid spilt instantaneously
- a wreck scenario: 500 tonnes of sulphuric acid spilt continuously over 5 hours (100 t/h)
- a port scenario (Cherbourg): 100 tonnes of sulphuric acid spilt instantaneously
- a river scenario: 20 tonnes of sulphuric acid spilt continuously over 5 hours (4 t/h).

The scenarios

Channel scenario

- Location 50°N, 3°W
- Spill depth: 1 m
- Air and water temperature: 10°C
- Channel currents
- Duration of spill: - 5 hours
- instantaneous

Wreck scenario

- Location 49°27N; 3°15W
- Spill depth: 87 m
- Air and water temperature: 10°C
- Channel currents
- Duration of spill: 5 hours

Port scenario

- Depth of the port basin: 15 m
- Air and water temperature: 10°C
- Slow current
- Duration of spill: - instantaneous

River scenario

- Depth of river: between 4 and 5 m
- Width of river: 300 m
- Spill depth: 1 m
- Air and water temperature: 15°C
- Two current speeds: 0.12 m/s and 0.74 m/s
- Duration of spill: 5 hours

Modelling

CHEMMAP software was used to model hypothetical spillages of sulphuric acid in the aquatic environment.

This is a chemical spill model designed by ASA (Applied Science Associates, Inc - USA) which predicts the movement and fate of the spilt

product in fresh and sea water.

This model indicates both the movement of the product on the water surface and its distribution in the environment (evaporation, dissolution in the water column...). The time step used for the calculations is thirty minutes.



Results obtained after a spill of 500 tonnes of sulphuric acid in the Channel.



Figure 1
Location of the hypothetical spill in the Channel




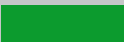







Figure 2
View of the dissolved part

-  Spill location
-  Sampling point

The CHEMMAP model does not take into account the buffering capacity of seawater. Graphs therefore had to be drawn up (cf. annex 1) in order to obtain the pH values in the aquatic environment according to the concentration of sulphuric acid spilt in this environment (cf. table below).

Concentrations of dissolved sulphuric acid and corresponding pH ranges in **seawater**

mg/m ³	seawater	g/L	pH
1 to 10		10 ⁻⁶ to 10 ⁻⁵	little change from initial pH
10 to 100		10 ⁻⁵ to 10 ⁻⁴	little change from initial pH
100 to 1000		10 ⁻⁴ to 0.001	little change from initial pH
1000 to 10000		0.001 to 0.01	little change from initial pH
10000 to 100000		0.01 to 0.1	7.5 < pH < 5.5
100000 to 1000000		0.1 to 1	6 < pH < 1.5
1000000 to 10000000		1 to 10	1.5 < pH < 0.5
10000000 to 100000000		10 to 100	< 0.5
> 100000000		> 100	< 0.5

8.5 < acceptable pH < 7

Table 1

Results of the Channel scenario

Acceptable pH ranges according to spill rate

* Maximum concentration of sulphuric acid obtained in the water column

** Concentration at which the pH of the water remains acceptable (greater than 7) – see table 1, page 22.

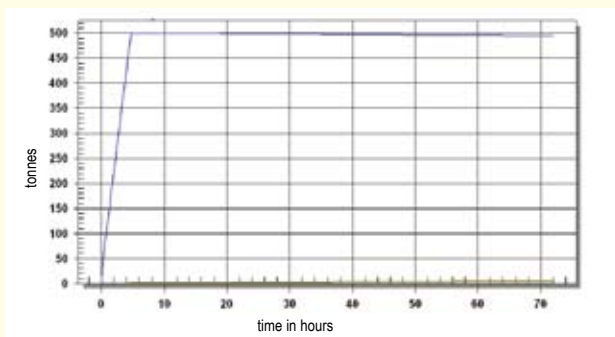
Spill rate	Concentration of sulphuric acid dissolved in the water column	Time after spill	Distance from spill location (taking into account the movement of the water mass according to the tide)
10 kg/h over 5h	$C_{max}^* = 70 \text{ mg/m}^3$	45 min	500 m
1 000 kg/h over 5h	$C_{max} = 7,000 \text{ mg/m}^3$	30 min	530 m
100 t/h over 5h	$C_{max} = 720,000 \text{ mg/m}^3$	15 min	500 m
	$C_{accept}^{**} = 100,000 \text{ mg/m}^3$	5h15	1 600 m
500 t instantaneously	$C_{max} = 16,000,000 \text{ mg/m}^3$	15 min	570 m
	$C_{accept} = 100,000 \text{ mg/m}^3$	8h30	10 km

Table 2

The 10 kg/h and 1,000 kg/h spill scenarios do not cause significant alterations to the pH in the surrounding area: the maximum concentrations measured remain well below 100,000 mg/m³ (concentration at which the pH is greater than or equal to 7). Consequently, only the results of the 100 t/h and the 500 t instantaneous spills will be examined.

Spill of 100 t/h of sulphuric acid over 5 hours in the Channel.

- Behaviour of the 100 t/h of sulphuric acid spilt over 5 hours, with a 3 m/s wind:



Graph 1

— Quantity evaporated
 — Quantity dissolved
 — Quantity on the surface

The sulphuric acid gradually sinks ($d = 1.84$) in the water column, whatever the quantity spilt.

• **Influence of the wind speed on the behaviour of the sulphuric acid spill:**

Wind speed	t + 24 h	t + 48 h	t + 72 h
3 m/s	140 km ²	165 km ²	230 km ²
10 m/s	1,000 km ²	1,800 km ²	3,000 km ²

Table 3 t = beginning of spill

The stronger the wind, the larger the surface area liable to be affected by the acid.

• **Behaviour of the 100 t/h of sulphuric acid spill over 5 hours, according to the wind speed**

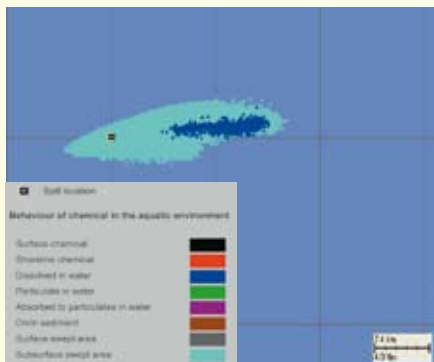


Figure 3

For a 3 m/s NW wind, the surface area likely to be affected will be 16 NM (29.6 km) long and 4 NM (7.4 km) wide for a period of 72 hours.

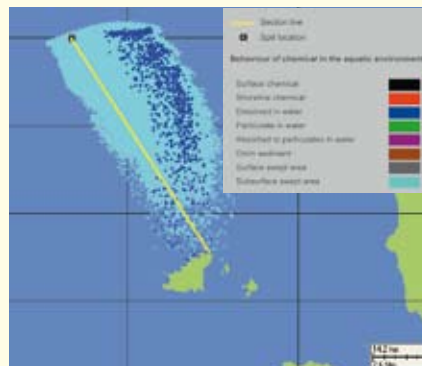


Figure 4

For a 10 m/s NW wind, the surface area likely to be affected will be 38 NM (70.2 km) long and 19 NM (35.2 km) wide for a period of 72 hours.

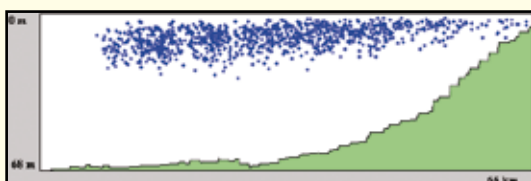


Figure 5

This diagram relates to figure 4 and indicates the depth of water mass affected by the acid, between 0 and 30 metres for a 10 m/s wind. The water mass is influenced by the wind.

• **Concentrations of sulphuric acid dissolved in the water column and areas where the pH is less than 7, according to the wind speed:**

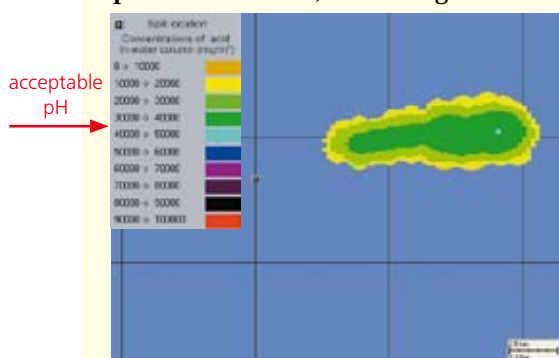


Figure 6

For a 3 m/s wind, the area where the pH is less than 7 spreads up to 14 km around the spill location and is detected up to 22 hours after the spill begins.

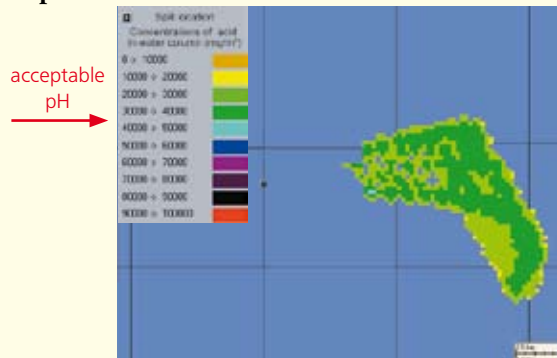


Figure 7

For a 10 m/s wind, the area where the pH is less than 7 spreads up to 6 km around the spill location and is detected up to 7 hours after the spill begins.

* Definitions in glossary

Instantaneous spill of 500 tonnes of sulphuric acid in the Channel

- **Influence of the wind speed on the behaviour of the sulphuric acid spilt:**

Wind speed	t + 24 h	t + 48 h	t + 72 h
3 m/s	85 km ²	100 km ²	150 km ²
10 m/s	780 km ²	1,200 km ²	1,850 km ²

Table 4 t = beginning of spill

The stronger the wind, the larger the surface area liable to be affected by the acid.

- **Behaviour of the 500 tonnes of sulphuric acid spilt instantaneously, according to the wind speed**

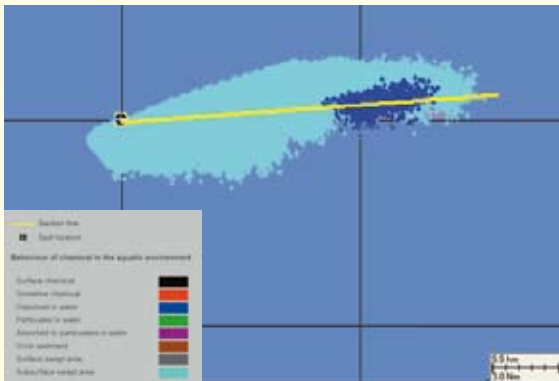


Figure 8

For a 3 m/s NW wind, the surface area likely to be affected will be 12 NM (22.2 km) long and 1.4 NM (2.6 km) wide for a period of 72 hours.

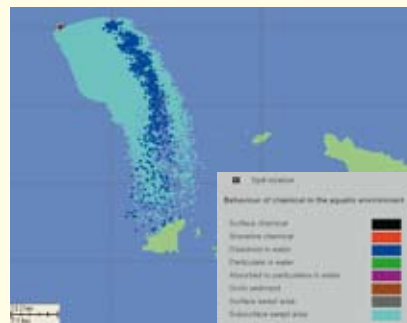


Figure 9

For a 10 m/s NW wind, the surface area likely to be affected will be 34 NM (63 km) long and 21.3 NM (39.4 km) wide for a period of 72 hours.

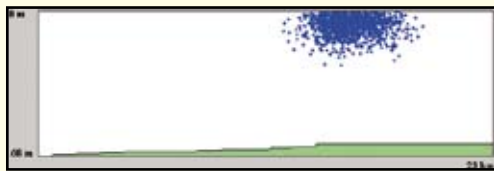


Figure 10

This diagram relates to figure 8 and indicates the depth of water mass affected by the acid, between 0 and 30 metres for a 3 m/s wind. The water mass is influenced by the wind.

- **Concentrations of sulphuric acid dissolved in the water column and areas where the pH is less than 7, according to the wind speed:**

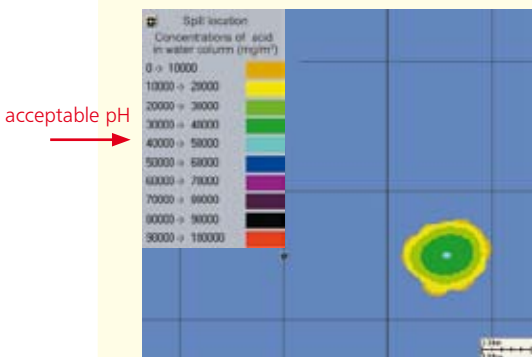


Figure 11

For a 3 m/s wind, the area where the pH is less than 7 spreads up to 12 km around the spill location and is detected up to 2.5 hours after the spill.



Figure 12

For a 10 m/s wind, the area where the pH is less than 7 spreads up to 16 km around the spill location and is detected up to 12 hours after the spill.

Results of the wreck scenario

A wreck is lying on the seabed 87 m below the surface not far from an inhabited coastline and begins to leak.

The leak causes the **continuous release of 500 tonnes of sulphuric acid over 5 hours from the tanks of the wreck.**



Figure 13

Location of the wreck

Continuous spill of 500 tonnes of sulphuric acid over 5 hours from the seabed

- Concentrations in the affected water column, between 73 and 87 m (figure 15), obtained **30 minutes** after the acid is released:

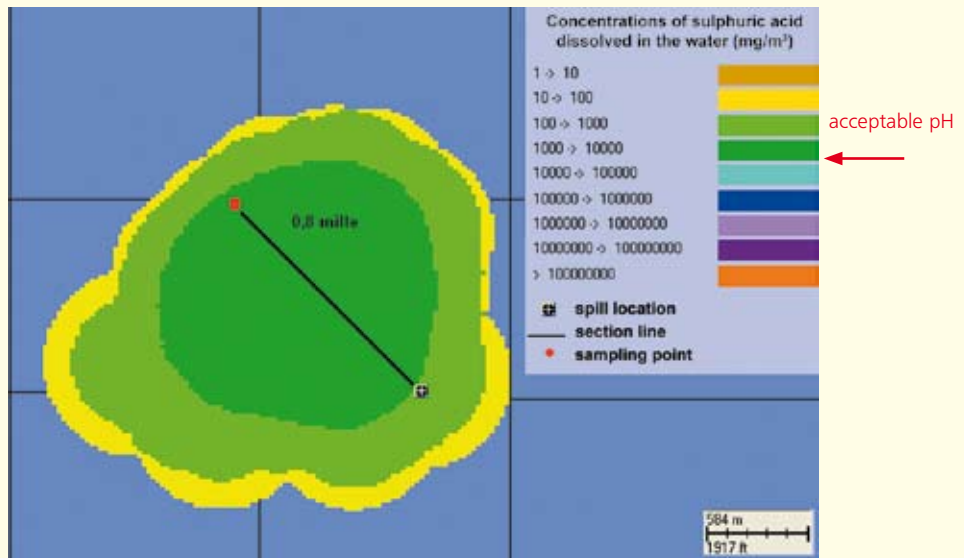


Figure 14

Average and maximum concentrations at the sampling point

	Average concentration (g/L)	Expected pH	Maximum concentration (g/L)	Expected pH
Up to 0.8 NM NW of the spill location	0.007	7.8	0.0125	7.6

Table 5

Concentrations of sulphuric acid along the section line (in black, figure 14)

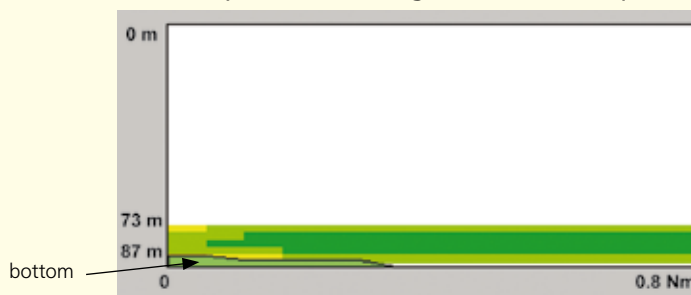


Figure 15

The acid released dissolves gradually but remains largely on the seabed.

- Behaviour of sulphuric acid **48 hours** after the release from the wreck: dissolution in the water column (in yellow) and course taken by the acid (in blue) 48 hours after the spill begins:

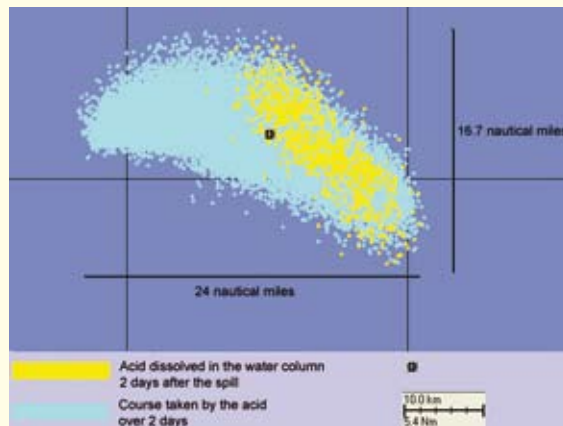


Figure 16

- Average concentrations obtained **48 hours** after the acid is released:

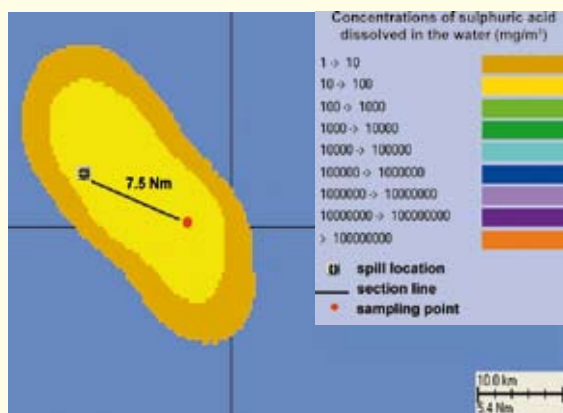


Figure 17

acceptable pH

Concentrations of sulphuric acid along the section line (in black, figure 17)

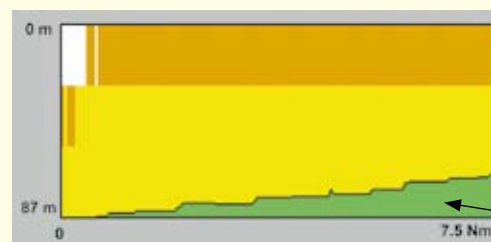


Figure 18

bottom

Average and maximum concentrations at the sampling point

	Average concentration (g/L)	Expected pH	Maximum concentration (g/L)	Expected pH
Up to 7.5 NM ESE of the spill location	0.0002	8	0.0125	7.6

Table 6

Results of the port scenario

Instantaneous spill of 100 tonnes of sulphuric acid on the surface, with no wind and a current speed of naught.

- Behaviour of sulphuric acid **48 hours** after the release at the surface: dissolution in the water column (in dark blue) and course taken by the acid (in pale blue) 48 hours after the spill begins:

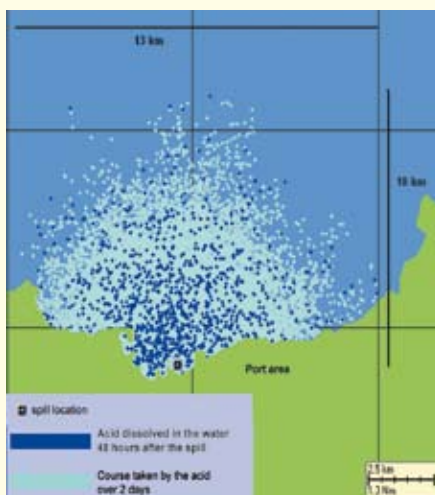


Figure 19

The area affected spreads 10 km north and 13 km from east to west. The acid sinks to the bottom and dissolves in the water column. The average concentrations of sulphuric acid 48 hours after the spill are around 0.035 g/L, which corresponds to a pH of 7.3. The pH can drop as low as 6.2.

- Analysis of concentrations and pH values:

Average and maximum concentrations at several sampling points

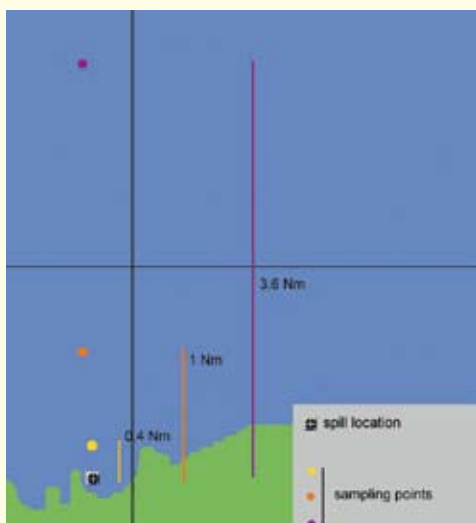


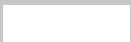






Figure 20

Distance from spill location to sampling point	Average concentration (g/L)	pH	Maximum concentration (g/L)	pH
0.4 Nm (impacted 30 minutes after spill)	0.0175	5.5	0.08	1.8
1 Nm (impacted 9.5 hours after spill)	0.0008	7.5 (little variation)	0.08	1.8
3.6 Nm (impacted 15 hours after spill)	0.000025	8 (no variation)	0.08	1.8

Table 7

Results of the river scenario

Concentrations of dissolved sulphuric acid and corresponding pH ranges in fresh water

mg/m ³	fresh water	g/L	pH
1 to 10		10 ⁻⁶ to 10 ⁻⁵	little change from initial pH
10 to 100		10 ⁻⁵ to 10 ⁻⁴	little change from initial pH
100 to 1000		10 ⁻⁴ to 0.001	little change from initial pH
1000 to 10000		0.001 to 0.01	little change from initial pH
10000 to 100000		0.01 to 0.1	7 < pH < 5.5
100000 to 1000000		0.1 to 1	5.5 < pH < 1.8
> 1000000		> 1	< 1.8

8 < acceptable pH
< 5.5



Table 8

Continuous spill over 5 hours of 20 tonnes of sulphuric acid (spill rate = 4 t/h), with a current speed of 0.12 m/s or 0.74 m/s.

- Influence of the current:**

Current speed	Maximum distance at which a variation in pH is observed in 24 h
0.12 m/s	1.31 km downstream
0.74 m/s	5 km downstream

Table 9 t = beginning of spill

The surface area liable to be affected is larger when the current is stronger.

- **Maximum concentrations of sulphuric acid obtained according to the current speed:**

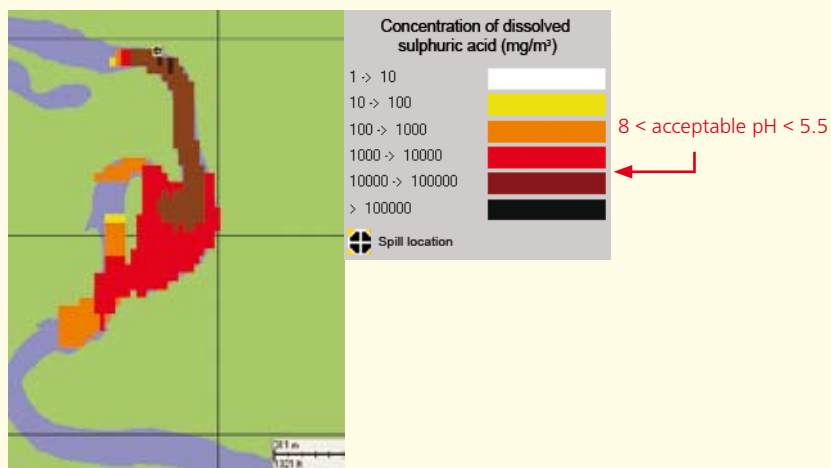


Figure 23

With a **0.12 m/s current**, 3 hours after the spill, the area in which the pH is less than 5.5 spreads 80 m downstream of the spill location. Three days after the spill, the pH returns to a value greater than 5.5 (pH value considered acceptable for the environment).

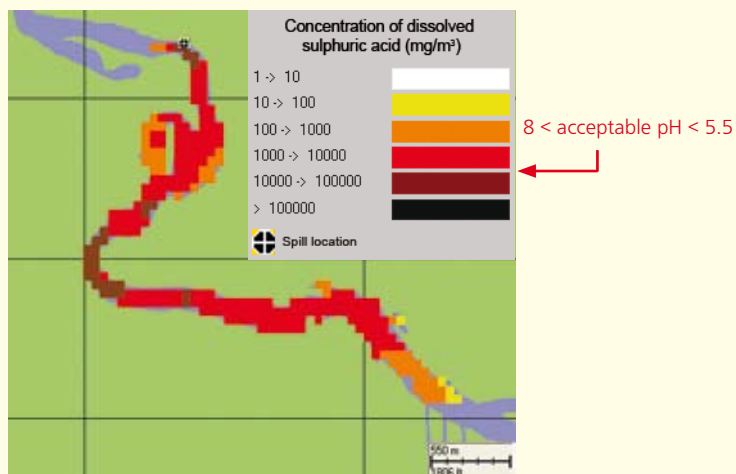


Figure 24

With a **0.74 m/s current**, 3 hours after the spill, the area in which the pH is less than 5.5 spreads 2 km downstream of the spill location. Three days after the spill, the pH returns to a value greater than 5.5 (pH value considered acceptable for the environment).

Consumption scenarios

As sulphuric acid does not bioaccumulate along the food chain, it will therefore not be found in aquatic organisms in high enough concentrations to have an impact on consumers of exposed sea produce.

Response

- Experience feedback _____ **D1**
- Examples of sulphuric acid spills _____ **D2**
- Response recommendations _____ **D3**
- Response techniques _____ **D4**
- Choosing personal protective equipment (PPE) _____ **D5**
- Measuring devices and waste treatment _____ **D6**



Experience feedback

Collision of *ENA 2* in a port (Germany, June 2004)

ENA 2 is a 62 metre long, double hulled barge, containing four 125 m³ tanks. On 28 June, *ENA 2* was transporting 500 tonnes (920 m³) of concentrated sulphuric acid from an industrial terminal in the port of Hamburg to a warehouse located a few nautical miles downstream of the Elbe, when she hit the containership *Pudong Senator*, a 294 metre long vessel with a capacity of 4,545 containers (twenty foot equivalent units). Thirty-five minutes after having berthed at her destination terminal, *ENA 2* capsized, without causing any casualties.

Emergency response

No indication of the volume of acid spilt into the water was available and the Hamburg fire service determined the safety perimeters: an exclusion area 100 metres around the vessel and a contamination reduction area 800 metres around the vessel (applicable to shipping traffic). Teams equipped with protection, pH-meters and thermometers mapped the aquatic area and sampled the atmosphere.

Risk assessment

The low variations in pH and the water temperature led the authorities to think that the acid was only leaking from the vessel's eight tank vents. However, if the acid were to flow out of the tanks simply to equalise the pressure difference, water would enter the tanks, diluting the acid in the tanks and thus increasing its activity, and therefore its corrosiveness, and causing the formation of hydrogen in the tanks. Eight people complained of irritations and were taken to hospital, fortunately without any serious repercussions.

Water canons were set up to prevent all risks of dispersion of gases and corrosive vapours.

The day after the accident, a 600 tonne floating crane, provided by the shipowner, was sent from Bremerhaven to Hamburg. The

pH around the wreck varied between 4 and 6, indicating that acid had indeed leaked out of the wreck.

Securing the wreck

Equipment was brought together (pumps, hoses, reception tanks). PH-meters were fixed to the divers' helmets and each dive was restricted to a maximum of 30 minutes. A tug agitated the water to promote the dilution of the acid in the natural environment and prevent the acid from accumulating in particular areas.

On Wednesday 30 June, 3 days after the incident, the upturned hull sat higher in the water, indicating the production of hydrogen and loss of acid through the vents which, according to calculations, could theoretically allow the leakage of 25 m³/h of acid. The floating pontoon arrived from Bremerhaven very early on Thursday morning. It became apparent that the manholes in two of the tanks were open and the vents of the two others had allowed the release of a lot of the acid. When determining how to ensure that the wreck was safe before turning it over, the responders were faced with a situation involving four tanks containing a large volume of explosive gas.

On the Friday, 5 days after the incident, the wreck was returned to an upright position after inerting. While the wreck was being turned over, a water curtain ran permanently so as to beat down any corrosive vapours and prevent sparks.



Turning over the *ENA 2*

Sulphuric acid spill from the *Balu* in the open sea (Bay of Biscay, March 2001)

On 20 March 2001, the Maltese chemical tanker the *Balu* was transporting a cargo of 8,021 tonnes (15,000 m³) of sulphuric acid when she sank in the Bay of Biscay, 220 km off Cape Finisterre (Spain) and 350 km from the Pointe de Penmarc'h (Southern Finistère, France). The vessel sank in waters 4,600 metres deep.

No operation to recover the acid was envisaged, only a survey of the spill area was carried out. The sulphuric acid released in the ocean gradually sank and dissolved. An exothermic reaction with water occurred but thermal dispersion in the ocean reduced any possible increase in temperature. The possible danger was related to the acidity of the water, measured by the pH. However, fishing was not affected by the spill (too deep and not the fishing season). Tests were conducted on water samples by the Spanish maritime authorities.

***Bahamas* spill in a port (Brazil, August 1998)**

On 24 August 1998, the tanker *Bahamas* entered the port of Rio Grande in Brazil loaded with 19,000 tonnes of 95% sulphuric acid.

Due to technical errors and a crisis situation caused by the vessel's dilapidated state, the machine room was flooded with a mixture of water and acid. This very corrosive mixture created serious problems for the vessel's structure. On 30 August, the vessel was listing significantly and the acid reached the main generators. The crew then evacuated the *Bahamas* for fear of explosion.

Jets of pressurised liquid were seen coming from the tanks and the pump room, made up of a mixture of acid and water. An attempt was made to pump the cargo to land, an operation ordered by the shipowners and conducted by SMIT TAK; however the mixture of acid and water was too corrosive and destroyed the hose used for pumping.

The problems for response were:

- the high risk of explosion due to the formation of hydrogen
- the absence of a tank on land to transfer the corrosive water and acid mixture into
- corrosion of the vessel's structure liable to cause leaching of heavy metals in the environment
- the fact that the incident occurred in a port: in practice it was impossible to neutralise such a large quantity of acid.

On 22 October 1998, a decision was made to slowly discharge the cargo into the port at falling tide, while constantly monitoring the pH. This pumping operation lasted more than eleven days, without ever exceeding the pH limits agreed on and without the leaching of ferrous compounds from the hull.

By 20 April 1999, the vessel had been emptied and was scuttled in international waters on the orders of the maritime authorities.

Examples of sulphuric acid spills

Sulphuric acid spill in Texas, Chocolate Bay (USA, August 2005)

On 15 August 2005, a barge containing 1,572 m³ of sulphuric acid grounded in a marshy bay in Texas. Measurements of the pH taken around the grounded vessel indicated the presence of sulphuric acid in the water: around 1,300 m³ of acid were spilt into the estuary. On 19 August, the acid and water mixture remaining within the barge was pumped out of the tanks. The ecological impact of this incident remains to be established, bearing in mind that the bay constitutes an important natural reserve. Fortunately, there were no casualties.

Collapse of a storage tank (Sweden, February 2005)

On 4 February 2005, a tank of sulphuric acid collapsed in a chemical plant in the harbour area of Helsingborg, in the south of Sweden. An estimated 11,000 tonnes of acid escaped from the storage tank. Part of the acid spread out into the sea, causing an exothermic reaction with the water and forming a cloud over the plant. An exclusion area was set up and a shelter-in-place was ordered, affecting the 110,000 local inhabitants. In all, 13 people were affected by slight breathing difficulties and eye irritation. The wind, blowing in the direction of the sea, promoted the dispersion of the cloud. It later became apparent that the accident was caused by a burst pipe flooding the ground on which the acid storage tank was standing, weakening the ground and thus causing the tank to collapse.

Leak from a tank onboard the *Panam Perla* (USA, November 1998)

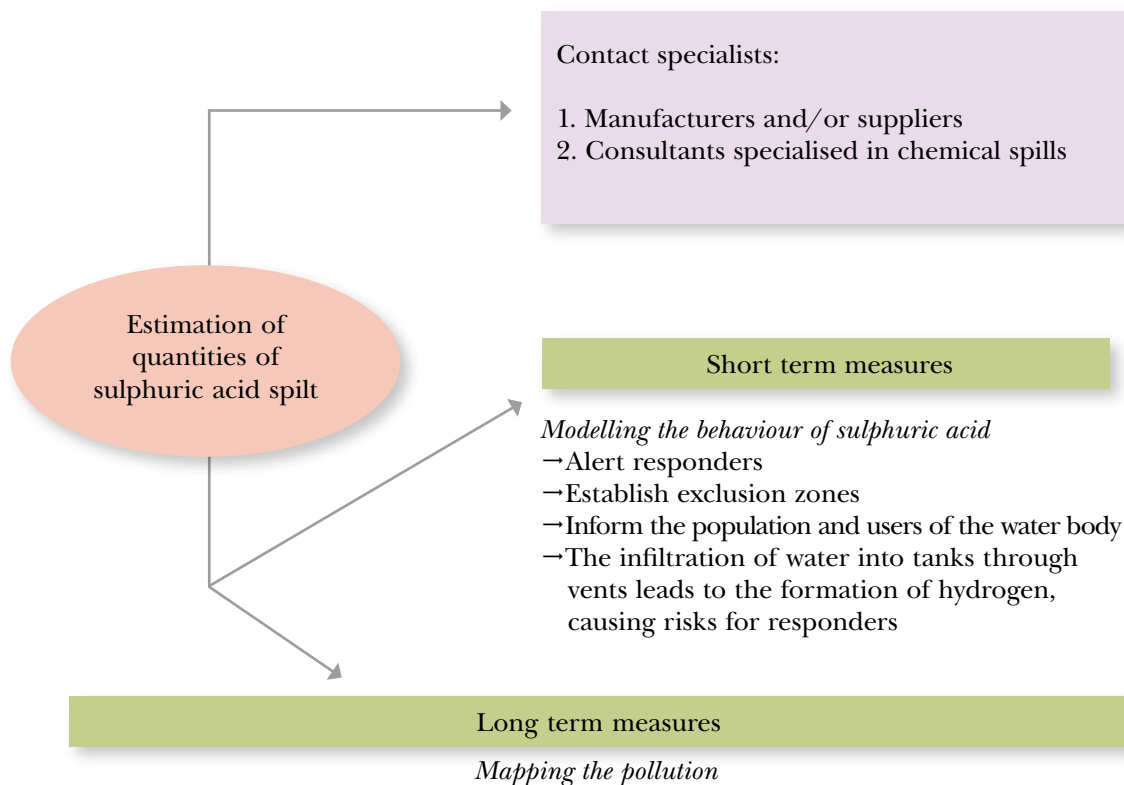
On 10 November 1998, one of the tanks of the *Panam Perla*, in the Atlantic, began to leak sulphuric acid, as its watertight seal failed. A recovery operation was conducted by pumping 100 tonnes (184 m³) of acid out of the double hull. The operation was completed one week after the leak was detected. The rest of the acid was neutralised by bicarbonate of soda.

Derailing of a rail convoy (Canada, 1995)

As a result of the derailing of a 44 carriage-train, 14 carriages were overturned onto the banks of Lake Masketsi in La Mauricie National Park. In total, 230 m³ of concentrated sulphuric acid sank to the bottom of the lake, approximately 33 metres deep. An exclusion area was set up 450 metres around the spill location and access to the surrounding area was controlled. The water from the lake was banned from consumption. The spill caused an "acid shock", which was fatal for all the fauna in the river for a stretch of over ten kilometres. The water's pH reached 2.5. More than 660 tonnes of calcium carbonate were released into the river and the lake to bring the pH back up to an acceptable value. The sulphuric acid did not spontaneously mix with the water but sank to the deepest parts of the lake. This behaviour allowed environmental experts to constantly monitor the acid concentration.

Response recommendations

Diagram showing response actions in the event of a spill into a water body



D3

→ In the water column

- Measure concentrations
- Regularly monitor the pH and water temperature
- Establish exclusion zones (fishing, water intakes)
- Ecological monitoring
- Neutralisation in confined areas without currents, possibly offsite (rare situations)

→ On the bottom (wreck)

- Type of sediments
- Topography
- Currents
- Water temperature
- Estimate dilution, if recommended to empty the wreck, to keep the environmental impact to a minimum.

→ In the atmosphere

- Measure the air with specific detectors
- Protect responders
- Evacuation

Is response possible?

Response actions on a damaged vessel may be possible if the precautions outlined below are taken:

- Sulphuric acid may come into contact with water: either directly in the sea, which will rapidly dilute acid concentrations and reduce heat production; or onboard the vessel, for instance in storage tanks. In this case, the reaction will be violent and dangerous. This exothermic reaction may cause projections of liquid (water and acid mixture). Sulphuric acid, in the presence of heat or humidity/water, may react with the steel of the hull and the tanks and give off hydrogen. When heated, the acid will produce corrosive and irritating fumes.
- Approach the accident area from upwind (wind behind you), equipped with personal protective equipment (PPE). The number of responders in the risk area should be kept to a minimum.
- Set up a water spray if there is a risk of hydrogen production.
- In theory, the action of sulphuric acid could be neutralised in shallow waters and in limited quantities using bicarbonate of soda. However, no example of this type of application exists. Furthermore, when a freight train transporting sulphuric acid was derailed in Canada in 1995, it was reported that the concentrated acid sank into the shallow waters and did not spontaneously mix with the water.

Emergency measures in the event of a leak or spill

- Ban access to the spill location and prohibit the use of polluted waters. Write "CORROSIVE" on signs.
- Use breathing apparatus and facial protection and wear a hazmat suit.
- Stop or reduce the leak if doing so does not constitute a risk.
- Avoid all direct contact with the product and do not inhale vapours.
- Use fireproof materials.

Emergency response in the event of fire

- Cool the receptacles/tanks by spraying with water.
- Beat down gases/fumes/dust by spraying with water.
- Eliminate all sources of sparks or ignition. Do not smoke.
- Ensure that no water leaks into the containers of acid.
- The fire extinguishers which can be used will depend on the products on fire. Use an aqueous film-forming foam (AFFF), or for small fires carbon dioxide or chemical powder. **If only water is available, use it in the form of a mist.**

Transshipment

- Sulphuric acid must be unloaded from tanks with extreme caution. Provide storage tanks for the acid or possible acid and water mixture, as well as pumps made of cast iron with a high silicon content or centrifugal pumps made of alloy 20.
- Approach the spill location upwind and keep the wind behind you throughout response, paying particular attention to any projections of liquid, equipped with breathing apparatus and hazmat suits.
- If hydrogen is formed, the tanks can be emptied by pumping, using an inert gas such as nitrogen. It is essential to inert tanks before pumping.

Response techniques

Response

(FICHE RÉFLEXE D'INTERVENTION ANTIPOLLUTION "PRODUITS DANS LA COLONNE D'EAU ET SUR LE FOND : LIQUIDES SOLUBLES ET COULANTS", FICHE GUIDE N°3 : "LUTTE EN MILIEU AQUATIQUE", FICHES STRATÉGIES ET MOYENS N°4,5,8,9,13. CEDRE, 2004)

On land

It is essential to intervene as rapidly as possible in order to prevent any polluted water from reaching drains or a waterway, by containing the acid spill with dams made of earth, sand or other materials or by deflecting it towards an impermeable surface.

Inland waters

As sulphuric acid is highly soluble in water, it is difficult to respond to a spill in water. Where possible, deflect polluted waters immediately after the spill for subsequent storage and treatment. If the polluted water cannot be deflected, a possible response option is to promote dilution. Dilution may occur naturally (for instance in the case of a small stream flowing into a larger river with a faster flow). The pH of the aquatic environment and the temperature must be monitored in the case of an acid spill.

Calm, shallow waters

Water intakes must be closed off and the evolution of the pH and water temperature regularly monitored. The polluted water mass may be pumped off for treatment in an appropriate treatment plant. Accumulation of the acid can also be prevented by promoting dilution (agitation of the water mass by propellers).

At sea

It is important to stop the leak and the flow into the aquatic environment if this is possible and not dangerous. The role of natural dilution must be taken into account in the case of a spill at sea, as well as the buffering capacity

of seawater in the event of an acid spill. The environment must be monitored by regularly measuring the pH and temperature.

Pay particular attention to spray in the air, due to mixtures of acid and water, as well as the release of large amounts of heat.

In adverse weather conditions, acid vapours can be transported over long distances by the wind. Except in a few rare cases (e.g. harbour basins with no current), it is impossible to recover the polluted water.

If the polluted water is even partially recovered by pumping, it may be neutralised. This involves bringing the pH of the polluted water mass back as close as possible to its usual value. This can be carried out using two different methods: either by natural dilution in a large water mass (release at sea) or by adding a neutralising agent such as bicarbonate of soda (NaHCO_3). This second possibility can only be conducted for small or moderate volumes of pollution due to the quantity of agent needed (2 to 3 times the mass of the product spilt). The agent is added using a fire hose or by directly applying it from the container.

Finally, it is useful for responders to understand the behaviour of sulphuric acid in the water column. This behaviour can be modelled using the CHEMMAP model for the simulation of chemical spills (see the "Accident scenarios" chapter).

Choosing personal protective equipment (PPE)

Ensure maximum protection in the case of unknown or high concentrations of sulphuric acid.

Choosing breathing apparatus (FINGAS, 2000)

According to maximum use concentrations (MUC)²:

- Gas mask for up to 4 ppm.
- Self-contained breathing apparatus (SCBA) above 4 ppm.

At normal temperatures, concentrated sulphuric acid gives off invisible vapours. It is therefore important to wear eye protection and breathing apparatus when handling this acid.

Choosing protective clothing

(CEFIC ERICARD, 2003)

In all cases, a hazmat suit must be worn, as well as facial protection (full safety goggles). Gloves are also recommended (neoprene or PVC, see table on page 41).

Wash contaminated protective clothing and breathing apparatus with water before removing the face mask and protective suit and place them in containers provided for this purpose. Wear protective clothing and self-contained breathing apparatus when helping other responders to remove their protective clothing and when handling contaminated equipment.

Recommendations for use in the event of a spill (FINGAS, 2000)

- Pressure demand open-circuit SCBAs give the best safety protection. Their protection factor is around 10,000 (e.g. ELV = 0.75 ppm, protection up to 7,500 ppm of sulphuric acid in ambient air temperatures).

- Use an air-supplied respirator to enter an area with unknown concentrations, as concentrated sulphuric acid gives off invisible toxic vapours at ambient temperatures.
- An air-purifying respirator can be used in a stable situation where the concentration of acid does not reach the IDLH value and is unlikely to increase.
- Warning: certain facial characteristics such as a scar, a narrow face shape or facial hair may lead to poor adjustment of the mask and impair the level of protection.
- In warm weather: excessive perspiration reduces the effectiveness of the watertight seal between the mask and the skin.
- In cold weather: ice may form on the regulator and the mask may steam up.
- Warning: ordinary glasses cannot be worn under the mask; special frames exist. However, contact lenses are permitted with new models of masks which allow gas exchange as the lenses therefore do not dry out or stick to the eye.
Mask adjustment tests are recommended for new users and regular tests for other users.

D5

² Maximum use concentrations can vary according to the make and model. Contact the manufacturer for more information.

Measures to be taken after using PPE in a spill situation

- Decontaminate boots after response. A foot bath and mild detergent can be used. Do not forget to treat the contaminated water.
- Decontaminate gloves separately from boots in a bucket with a mild detergent.
- Only reuse protective suits if they have been cleaned.

Permeation times through different materials (FORSBERG ET KEITH, 1995)

BETEX (butyl/neoprene): > 360 min
 Butyl: > 480 min
 Natural rubber: 80 min
 Neoprene: > 360 min
 Nitrile: 10 min (variable)
 Polyvinyl chloride: 10 min (variable)
 Teflon: no data available.
 Viton: > 240 min

Chemical resistance

Material	Breakdown	Permeation	Use
Nitrile			not recommended
Neoprene	Moderate	permeation time: 105 minutes	suitable as long as use is closely controlled
Polyvinyl alcohol (PVA)			not recommended
Polyvinyl chloride (PVC)		permeation time: 3.6 hours	suitable as long as use is closely controlled
Natural rubber			not recommended
Linear low density polyethylene (LLDPE)	no breakdown tests have been carried out but should be good or excellent as the permeation time is > 8 hours	permeation time: > 480 minutes	appropriate

Note: this chemical resistance table is intended simply to give an indication of relative values. An assessment in the real conditions of usage should be carried out.



Measuring devices and waste treatment

Measuring devices

- **Methods of detection and measurement in water:** pH meter, thermometer.
- **Methods of detection and measurement in air** (INRS, 1997):
 - Dräger detection system using sulphuric acid indicator tube 1/a
 - air sampling tube containing silica gel, dosage by ion chromatography after desorption with an eluent
 - sampling using PVC air sampling filters (aerosols) used in conjunction with cellulose filters impregnated with sodium carbonate (gaseous pollutants), dosage by ion chromatography.

Addresses of special industrial waste treatment plants in France

The organisations able to treat this type of waste are listed at the following address:
<http://www.observatoire-dechets-bretagne.org>
(French only).

Examples of European manufacturers of sulphuric acid

 (ECB, 2005)

ARKEMA, Hœchst, WITCO, BASF.

Further information

- Glossary ————— E1
- Acronyms ————— E2
- Useful websites ————— E3
- Bibliography ————— E4

Glossary

Acceptable Daily Dose (ADD)

For humans this dose is the quantity of a substance that can be ingested by an organism per day for its entire lifetime without presenting a health hazard for the organism in question.

Acute Exposure Guideline Levels (AEGs)

Defined by the National Research Council's Committee on Toxicology (USA), AEGs are three levels above which the general population may experience certain effects. These three AEGs are given for five exposure times: 10, 30 min, 1, 4 and 8 hours.

AEGL 1: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non sensory effects. However, the effects are transient and reversible when exposure ceases.

AEGL 2: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

Adsorption

Elevation of the concentration of a substance dissolved at the interface of a condensed phase and a liquid phase under the influence of surface forces. Adsorption can also occur at the interface of a condensed phase and a gas phase.

Aerosol

A mass of particles, solids or liquids in suspension in a gaseous environment.

Bioaccumulation

Continued retention of a substance in the tissue of an organism throughout the course of its existence (the bioaccumulation factor increases all the time).

Bioamplification

Retention of a substance in the tissue at increasingly higher concentrations the higher one goes in the food chain.

Bioconcentration

Retention of a substance in the tissue of an organism to the extent that the content of the substance in the tissue exceeds that found in nature at one point in the lifetime of the organism.

Bioconcentration factor (BCF)

Ratio of the chemical concentration in the exposed organism (minus the concentration in a control organism) to that in surrounding water.

Biotransformation

Biological transformation of substances in a living organism via enzymatic processes.

Boiling Liquid Expanding Vapour Explosion (BLEVE)

A violent vapour explosion of a liquid that is significantly above its usual boiling point at atmospheric pressure after a tank has burst.

Boiling point (measured at a pressure of 1 atmosphere)

Temperature at which a liquid begins to boil. More specifically, when the temperature at which saturating vapour pressure of a liquid is equal to standard atmospheric pressure (1,013.25 hPa). The boiling point measured depends on atmospheric pressure.

Buffering capacity

Capacity of a solution to absorb a certain quantity of acid or base without causing a significant variation in pH. In the marine environment, the buffering capacity is due to the dihydrogenocarbonate/carbonate balance.

Combustion rate

Rate at which an object subjected to fire will burn entirely.

Critical point

Point at which the temperature and pressure at which the intensive properties of a liquid and vapour (density, calorific value...) are equal. It represents the highest temperature (critical temperature) and pressure (critical pressure) at which a gas phase and a liquid phase of a given compound can coexist.

Critical pressure

Maximum pressure for which the distinction can be made between a gas and a liquid.

Critical temperature

Temperature at which, when boiling, there is no longer any clear cut transition between the liquid and the gas state.

Daily exposure dose

Dose (internal or external) of a substance in an organism compared to the weight of the individual and the number of days of exposure (in the case of a non carcinogenic substance) and the number of days lived by the organism (for a carcinogenic substance).

Decomposition products

Products stemming from chemical or thermal disintegration of a substance.

Diffusion coefficient in air (and in water)

A constant that describes the movement of a substance in the gas phase (or liquid phase) in response to a concentration differential in the gas phase (or liquid phase).

Effective concentration 50 (EC₅₀)

Concentration causing a given effect (mortality, growth inhibition...) for 50% of the population under consideration during a given period of time.

Emergency Response Planning Guidelines (ERPG)

The American International Health Alliance (AIHA) set three maximum concentrations in 1988 below which a category of effects is not expected for an exposure duration of one hour, in a bid to protect the general public.

ERPG1: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly identifiable odour.

ERPG2: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to protect themselves.

ERPG3: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

Exposure limit value (ELV)

Ceiling exposure value measured for a maximum duration of 15 minutes.

Flash point

The lowest temperature at which a substance generates vapours that ignite or burn immediately when in contact with a flame.

Foam

The foam layer absorbs most of the vapours, physically eliminates vapours and isolates the chemical from sunlight and ambient air which reduces the amount of heat and subsequent vaporisation.

Henry's law constant

Value indicating a substance's volatility (see graph on p. 41)

Immediately Dangerous to Life or Health (IDLH)

Level below which a worker can escape to safety in thirty minutes in the event of sudden exposure to a dangerous atmosphere, without respiratory protection and without impairing his ability to escape.

Irreversible effect threshold (IET)

Concentration, for a stated exposure duration, above which irreversible effects can occur in the exposed population.

Lethal effect threshold (LET)

Concentration, for a stated exposure duration, above which mortality can be observed in the exposed population.

Lower Explosive Limit (LEL)

Minimum airborne concentration above which vapours ignite.

Lowest Observed Effect Concentration (LOEC)

Lowest concentration at which an effect is observed.

Marine pollutant

Substance, object or matter likely to cause serious damage to the marine environment when spilled.

Maximum Allowable Relief Valve Setting (MARVS)

Indicates the maximum admissible calibration of pressure relief valves of a cargo tank.

Mean exposure value (MEV)

Value that has been measured or estimated for a work station lasting 8 hours and is intended to protect workers from long term effects. MEV can be exceeded for very short periods providing the ELV value (should there be one) is not exceeded.

Median lethal concentration (LC₅₀)

Concentration of a substance deduced statistically that should, during or after exposure and for a given period of time, cause the death of 50% of the animals exposed during a given time period.

Melting point

Temperature at which solid and liquid state coexist. The melting point is a constant for a pure substance and is usually calculated at standard atmospheric pressure (one atmosphere).

Minimum Risk Level (MRL)

This level is an estimate of daily human exposure to a chemical which probably has no appreciable risk of non-carcinogenic noxious effect on health for a specific exposure duration.

Miscible

Matter that mixes readily with water

Nautical Mile

1 nautical mile is the equivalent of 1,852 metres and corresponds to one minute of latitude.

N-octanol/water partition coefficient (Kow)

Ratio of the equilibrium concentrations of a substance dissolved in a two phase system made up of two solvents that virtually do not mix.

No Observed Effect Concentration (NOEC)

Concentration of a substance measured during chronic toxicity tests for which no effect is observed, meaning that the substance presents no chronic toxicity below this concentration.

No Observed Effect Level (NOEL)

The highest dose of a substance that causes no distinct changes as compared with those observed in control animals.

Olfactory threshold

Minimum air or waterborne concentration to which the human nose is sensitive.

Partition coefficient for organic carbon and water (Koc) (for organic substances)

Ratio of the amount of compound absorbed per unit mass of organic carbon in the soil or in a sediment and the concentration of the same compound in a water solution in a state of equilibrium.

Photo-oxidation

Oxidation of a chemical compound caused by exposure to light energy.

Polymerisation

This term describes the chemical reaction generally associated with the production of plastics. Fundamentally, the individual molecules of a chemical (liquid or gas) react together to form a long chain. These chains can be used for many applications.

Protective equipment

This refers to the respiratory or physical protection of a human being. Protection levels have been defined, including both protective clothing and breathing apparatus as accepted by response authorities such as the USCG, NIOSH and the EPA (US).

Level A: an SCBA (self contained breathing apparatus/respirator) and fully air and chemical-tight suit (that resists permeation).

Level B: an SCBA and a suit that protects against liquid spray (splash proof).

Level C: a full face mask or goggles and a suit that protects responders against chemicals (splash proof).

Level D: overalls without a respirator.

Rate of evaporation or volatility (ether = 1)

The rate of evaporation expresses the number of times that a product takes to evaporate as compared with a control substance of an equal volume (ether for instance). This rate varies with the nature of the product and the temperature.

Regression speed

Speed at which a burning liquid slick reduces in thickness. For a given liquid, this speed is constant regardless of the slick surface (slick diameter greater than 2 metres). Regression speed allows the total duration of a fire to be estimated if no attempt is made to extinguish it.

e.g. a 1,000 mm thick slick, where the regression speed is 10 mm/minute

duration of fire = $1000/10 = 100$ minutes.

Relative density

Ratio of the mass of a substance to that of water for a liquid or to that of air for a gas.

Relative vapour density

Weight of a volume of vapour or pure gas (without air) compared to that of an equal volume of dry air at the same temperature and pressure.

A vapour density lower than 1 indicates that the vapour is lighter than air and will have a tendency to rise. When the vapour density is higher than 1, vapour is heavier than air and will tend to stay near ground level and spread.

Self-ignition temperature

Minimal temperature at which vapours ignite spontaneously.

Solubility

Quantity of a substance dissolved in water. It will depend on salinity and temperature.

Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
ADD	Acceptable Daily Dose
ADNR	European Agreement concerning International Carriage of Dangerous Goods on the Rhine river
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
AEGLs	Acute Exposure Guideline Levels
AFFF	Aqueous Film-Forming Foam
AFSSA	French National Agency for Food Safety
AIHA	American International Health Alliance
ALOHA	Areal Locations of Hazardous Atmospheres
ATSDR	Agency for Toxic Substances and Disease Registry
AUV	Autonomous Underwater Vehicle
BCF	Bio Concentration Factor
BLEVE	Boiling Liquid Expanding Vapour Explosion
CAS	Chemical Abstracts Service
CEA	French Atomic Energy Commission
CEDRE	Centre of Documentation, Research and Experimentation on Accidental Water Pollution
CEFIC	European Chemical Industry Council
CHRIS	Chemical Hazards Response Information System
CSST	French Occupational Health and Safety Commission
CSTEE	French Scientific Committee on Toxicity, Ecotoxicity and the Environment
DDASS	French Departmental Health and Social Action Directorate
DDE	French Departmental Equipment Directorate
DRASS	French Regional Department of Health and Social Affairs
DRIRE	French Regional Directorates for Industry, Research and Environment
EC	Effective Concentration
ECB	European Chemicals Bureau
EFMA	European Fertilizer Manufacturers Association
EINECS	European Inventory of Existing Chemical Substances
ELV	Exposure Limit Value
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guidelines
ETC	Environmental Technology Centre
GP	Grande Paroisse
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IATA	International Air Transport Association
IBC	International Bulk chemical Code
ICSC	International Chemical Safety Cards
IDLH	Immediately Dangerous to Life or Health
IFREMER	French Research Institute for Exploitation of the Sea
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organization
INCHEM	International Chemical industries, Inc.
INERIS	French National Institute for Industrial Environment and Risks
INRS	French National Research and Safety Institute for occupational risk prevention
IPCS	International Programme on Chemical Safety
IPSN	French Institute for Nuclear Safety and Protection

IUCLID	International Uniform Chemical Information Database
LC	Lethal Concentration
LEL	Lower Explosive Limit
LET	Lethal Effect Threshold
LLDPE	Linear Low Density PolyEthylene
LOEC	Lowest Observed Effect Concentration
MARPOL	Marine Pollution
MARVS	Maximum Allowable Relief Valve Setting
MCA	Maritime and Coastguard Agency
MEV	Mean Exposure Value
MFAG	Medical First Aid Guide
MP	Marine Pollutant
MRL	Minimum Risk Level
MSDS	Safety Data Sheet
MUC	Maximum Use Concentrations
NIOSH	National Institute for Occupational Safety and Health
NM	Nautical mile
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
PEC	Predicted Effect Concentration
PID	Photo Ionisation Detector
PNEC	Predicted No-Effect Concentration
PPE	Personal Protective Equipment
ppm	Parts per million
PTBC	Para-tertiary-butylcatechol
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
ROV	Remoted Operated Vehicle
SCBA	Self-Contained Breathing Apparatus
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
SIDS	Screening Information Data Set
SIW	Special Industrial Waste
TEEL	Temporary Exposure Limits
TGD	Technical Guidance Document
TLV-ceiling	Threshold Limit Values – Ceiling
TLV-STEL	Threshold Limit Values - Short Term Exposure Limit
TLV-TWA	Threshold Limit Values - Time Weighted Average
TNO	Netherlands Organisation for Applied Scientific Research
TRANSAID	Agreement between UIC (French Chemical Industry Association) & the French Government
TROCS	Transport of Chemical Substances - database created by REMPEC
UEL	Upper Explosive Limit
UIISC	French Unit of Instruction and Intervention on Civil Security
US EPA	United States Environmental Protection Agency
UVCE	Unconfined Vapour Cloud Explosion
VCM	Vinyl chloride monomer
VHF	Very High Frequency
v/v	Volume to volume
WHO	World Health Organisation

Useful websites

AFSSA (French National Agency for Food Safety) (French only)

<http://www.afssa.fr>

ARKEMA

<http://www.arkemagroup.com>

ATSDR (Agency for Toxic Substances and Disease Registry)

<http://www.atsdr.cdc.gov/>

Bonn Agreement

<http://www.bonnagreement.org>

CEFIC (European Chemical Industry Council)

<http://www.ericards.net>

Chemfinder

<http://chemfinder.cambridgesoft.com>

CHRIS (Chemical Hazards Response Information System)

<http://www.chrismanual.com>

CSST (Occupational Health and Safety Commission)

<http://www.reptox.csst.qc.ca>

ETC (Environmental Technology Centre, Canada)

http://www.etc-cte.ec.gc.ca/etchome_e.html

European Chemicals Bureau

<http://ecb.jrc.it>

ICSC (International Chemical Safety Cards)

<http://www.cdc.gov/niosh/ipcs/ipccard.html>

INERIS (French National Institute for Industrial Environment and Risks)

<http://www.ineris.fr>

INRS (French National Research and Safety Institute for Occupational Risk Prevention)

<http://en.inrs.fr/>

IPCS (International Programme on Chemical Safety)

<http://www.who.int/ipcs/en>

NIOSH (US National Institute for Occupational Safety and Health)

<http://www.cdc.gov/niosh/>

NOAA (US National Oceanic and Atmospheric Administration), historical incident search page

<http://www.incidentnews.gov/>

TROCS REMPEC database (Regional marine pollution emergency response centre for the Mediterranean Sea) on transportation of chemicals

<http://www.rempec.org/databases.asp?lang=en>

UIC (French Chemical Industry Association)

<http://www.uic.fr/index-us.htm>

US Department of Energy, Chemical Safety Program, list of ERPGs

http://tis.eh.doe.gov/web/chem_safety/teel.html

US EPA (Environmental Protection Agency)

<http://www.epa.gov> (list of AEGLs)

Bibliography

Documents

ARKEMA. *Safety data sheet (SDS): Sulphuric acid 97 %*. 2003. 6 p. (SDS n° 18006, version 4)

ARKEMA. *Safety data sheet (SDS): Sulphuric acid 94/96/98 %*. 2003. 8 p. (SDS n° 02178, version 1)

ARKEMA. *Safety data sheet (SDS): Sulphuric acid 98 % purity*. 2003. 6 p. (SDS n° 00069, version 7)

CEDRE. *Fiche réflexe d'intervention antipollution "Produits dans la colonne d'eau et sur le fond : liquides solubles et coulants", Fiche Guide n°3 : "Lutte en milieu aquatique", Fiches stratégies et moyens n°4,5,8,9,13*. 2004.

CEFIC. *ERICards, Emergency Response Intervention Cards: transport of dangerous goods*. Brussels: Cefic, 2003. 322 p.

CHIMEDIT. *Guide international de la chimie 2004 et des sciences de la vie*. Paris: CHIMEDIT, 2004. 1238 p.

ENVIRONMENT CANADA (Environmental Protection Service). *Sulphuric acid and oleum*. Ottawa: Environment Canada, 1984. 100 p. (ENVIROGUIDE)

FINGAS, M. Personal protective equipment for hazardous material spill situations. *Spill technology newsletter*, January-December 2000, vol. 25, 13 p.

GRANDE PAROISSE. *Material safety data sheet (MSDS): Sulphuric acid 94-98 %*. 2003. 6 p. (MSDS n° GP-1160, version 6)

INRS. *Acide sulfurique*. Paris: INRS, 1997. 5 p. (Fiche toxicologique n°30)

IMO. *MARPOL 73/78: Consolidated Edition 2002: Articles, Protocols, Annexes, Unified Interpretations of the International Convention for the Prevention of Pollution from Ships, as modified by the Protocol of 1978 relating thereto*. London: IMO, 2002. 547 p.

IMO. *International code for the construction and equipment of ships carrying dangerous chemicals in bulk (IBC Code)*. London: IMO, 2001. 260 p.

LYMAN W.J, REEHL W.F, ROSENBLATT D.H. *Handbook of Chemical Property Estimation Methods*. Washington DC: American Chemical Society, 1990.

RECHENBACH P. *Le naufrage de l'alléger Ena 2 transportant de l'acide sulfurique concentré / Trad. de l'allemand par Hildegarde Kelly*. Hamburg: Sapeurs pompiers, 2004. 34 p.

TRANSPORT CANADA, U.S. DEPARTMENT OF TRANSPORTATION, SECRETARIAT OF TRANSPORT AND COMMUNICATIONS OF MEXICO. *1996 North American Emergency Response Guidebook: A Guidebook for First Responders During the Initial Phase of a Hazardous Materials/Dangerous Goods Incident*. Ottawa: Transport Canada, 1996.

Electronic information

Atmosphere, Climate & Environment Information Programme. *Freshwater wildlife and acidity* (page referred to in September 2006)

http://www.ace.mmu.ac.uk/eae/Figures/acid_wildlife.html

Canadian Centre for Occupation Health and Safety (page referred to in September 2006)

http://www.ccohs.ca/oshanswers/chemicals/chem_profiles/sulfuric_acid/basic_sa.html

CHRIS (Chemical Hazards Response Information System). *Material Safety Data Sheet* (page referred to in September 2006)

<http://www.chrismanual.com/S/SFA.pdf>

CSST (Occupational Health and Safety Commission). *Informations de la banque de données du Service du répertoire toxicologique sur l'acide sulfurique*. (page referred to in September 2006)

http://www.reptox.csst.qc.ca/Produit.asp?no_produit=174&nom=Acide+sulfurique (French only)

DIPPR L05. *Pure component thermodynamic properties database*. AICHE. Address: Prosim, Labège (France)

ECB (European Chemicals Bureau). *EINECS* (European Inventory of Existing Commercial chemical Substances) *information sheet on sulphuric acid*. (page referred to in September 2006)

http://ecb.jrc.it/esis-pgm/esis_reponse_self.php?GENRE=ECNO&ENTREE=231-639-5

ICSC (International Chemical Safety Cards). *International Chemical Safety Card on sulphuric acid*. (page referred to in September 2006)

<http://www.cdc.gov/niosh/ipcsneng/neng0198.html>

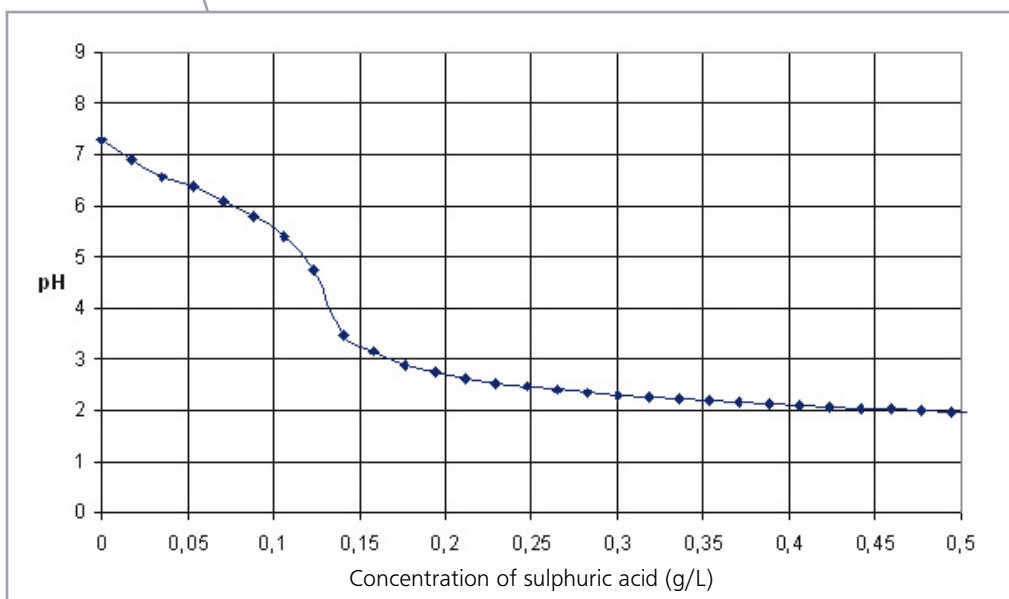
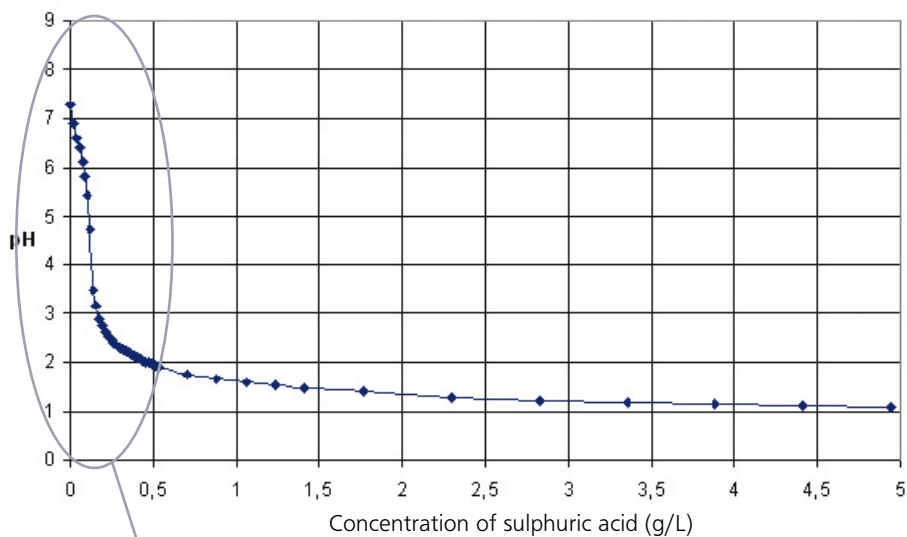
ANNEXES

- Annex 1: pH graphs
- Annex 2: summary and additional physical and toxicological data
- Annex 3: fax format data card
- Annex 4: classification of noxious liquid substances
(valid until 31/12/2006)
- Annexe 4b: new classification of noxious liquid substances
(valid since 01/01/2007)

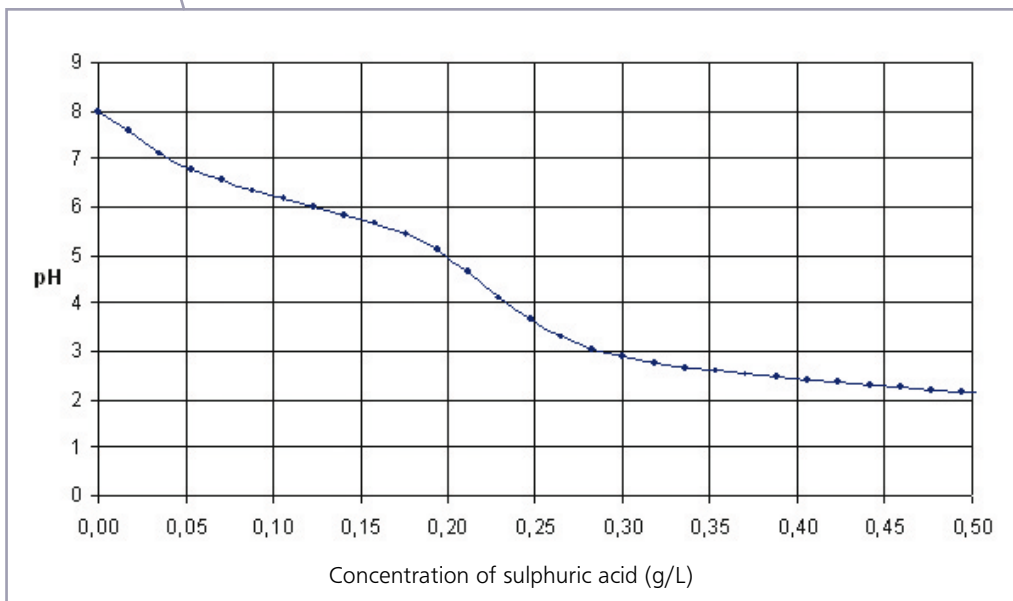
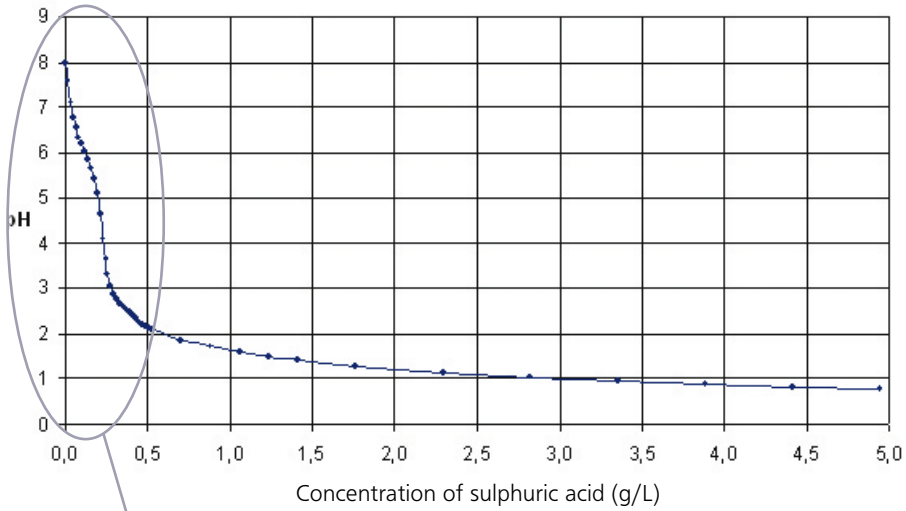
ANNEX 1: PH GRAPHS

pH values in the aquatic environment according to the concentration of sulphuric acid in the water

- Fresh water



- Seawater



ANNEX 2: SUMMARY AND ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

Classification

(CHRIS, 1999; INRS, 1997)

CAS n°:	7664-93-9
EC n° (EINECS):	231-639-5
UN n°:	1830
Index n°:	016-020-00-8
Class:	8

Physical data

Molar mass: 98.08 g/mol	INRS, 1997
Physical state at 20°C Appearance: oily Colour: colourless Odour: odourless	ENVIRONMENT CANADA ENVIROGUIDE, 1984
Solubility In fresh water: soluble in water at 20°C (with release of heat)	ARKEMA MSDS, 2003
In other compounds: soluble in ethyl ether and 1-butanol breaks down in ethanol	ARKEMA MSDS, 2003
pH of the solution: very acidic < 1 (94 to 98 %)	ARKEMA MSDS, 2003; G.P. MSDS, 2003
pK_a 1 st pK _a value < 0 2 nd pK _a value = 1.92	SIDS OCDE, 2001
Relative density (water = 1): 1.84 to 20°C (93 to 100 %)	SIDS OCDE, 2001
Vapour density (air = 1): 3.4	ICSC, 2000
Viscosity at 25°C: 21 mPa.S	ENVIRONMENT CANADA ENVIROGUIDE, 1984

Important temperatures

Boiling point at 1 atm:	335°C (98 %) 290°C (92 %)	ARKEMA MSDS, 2003 G.P. MSDS, 2003
Melting point:	10.49°C (98 %)	INRS, 1997
Freezing point:	-15°C (94 to 96 %) -10°C / +5°C (97 %) +5°C (98 %)	ARKEMA MSDS, 2003 ARKEMA MSDS, 2003 ARKEMA MSDS, 2003
Beginning of distillation:	304°C (94 to 96 %) 320°C / 335°C (97 %) 335°C (98 %)	ARKEMA MSDS, 2003 ARKEMA MSDS, 2003 ARKEMA MSDS, 2003
Self-ignition point:	non-flammable product	ENVIRONMENT CANADA ENVIROGUIDE, 1984
Latent heat of fusion:	9.8 kJ/mole (at melting point)	ENVIRONMENT CANADA ENVIROGUIDE, 1984

Other properties

Henry's law constant:	N/A	ENVIRONMENT CANADA ENVIROGUIDE, 1984
Diffusion coefficient in water:	N/A	
Diffusion coefficient in air:	N/A	
Surface tension at 20°C (with air):	55.1 mN/m	
Surface tension at 25°C (with air):	75 mN/m	
Olfactory threshold:	> 0.25 ppm (= 1 mg/m ³)	
Hygroscopic		

Vapour pressure/tension

< 0.001 hPa at 20°C	DIPPR, 2005
---------------------	-------------

Toxicological data

Sulphuric acid is a corrosive substance for the skin and mucous membranes upon contact; the intensity and nature of the lesions caused will depend on the concentration of the acid and the duration of exposure.

Threshold toxicological values

Occupational exposure values

MEV (France): 0.25 ppm (1 mg/m³)

ELV (France): 0.75 ppm (3 mg/m³)

TLV-TWA (ACGIH): 0.05 ppm (0.2 mg/m³)

Risk management values for the population

IDLH (NIOSH): 3.75 ppm (15 mg/m³)

TLV-STEL (ACGIH): data unavailable

TEEL 0: 0.25 ppm (1 mg/m³)

ERPG 1: 0.50 ppm (2 mg/m³)

ERPG 2: 2.50 ppm (10 mg/m³)

ERPG 3: 7.50 ppm (30 mg/m³)

Specific effects

Carcinogenic effects: a review of epidemiological studies tends to show a certain association between exposure to mists of strong inorganic acids containing sulphuric acid and the presence of cancer of the respiratory tract, and in particular laryngeal cancer and lung cancer.

Effects on fertility: no data available.

Teratogenic effects and/or effects on foetal development: not demonstrated.

Mutagenic effects: not demonstrated.

General toxicity

Acute human toxicity

- By ingestion: burns to the mouth and digestive tract with laryngeal oedema, vomiting of blood, possible perforation of digestive tract and a state of shock.
- By skin contact: severe burns.
- By eye contact: redness, pain, oedema, corneal opaqueness and possible loss of sight.

If concentrated solutions of sulphuric acid come into contact with the skin or eyes, they cause local caustic lesions if the affected area is not rapidly decontaminated.

- By inhalation: exposure to vapours causes coughing, breathing difficulties and can lead to bronchial irritation and pulmonary oedema in the presence of high concentrations. The effects are influenced by several factors including the particle size, the concentration of the product and the degree of humidity. Physical exercise can exacerbate symptoms.

Asthmatics are more sensitive to the bronchoconstrictor effects of inhaled acid.

Chronic human toxicity

- Repeated exposure by inhalation: dental erosion and chronic bronchitis.
- Irritant contact dermatitis can arise in the case of repeated contact with sulphuric acid or its solutions.
- The ACGIH (notation A2) and IARC (group 1) believe that exposure to mists of strong inorganic acid containing sulphuric acid is carcinogenic for humans.

Ecotoxicological data

Acute ecotoxicity

Crustacean (<i>Daphnia magna</i>)	EC ₅₀ (24h) = 29 mg/L (fresh water)
Fish (<i>Brachydanio rerio</i>)	LC ₅₀ (24h) = 82 mg/L (fresh water)
Fish (<i>Lepomis macrochirus</i>)	LC ₅₀ (48h) = 49 mg/L (fresh water)
Fish (<i>Pleuronectes platessa</i>)	LC ₅₀ (48h) = 100 to 330 mg/L (seawater)

Chronic ecotoxicity

Seaweed (<i>Gymnodium sp.</i>)	NOEC at pH 5.6 = 0.13 mg/L
Insect (<i>Tanytarsus dissimilis</i>)	NOEC (35 d) = 0.15 mg/L (fresh water)
Fish (<i>Jordanella floridae</i>)	NOEC = 0.025 mg/L (fresh water)
Fish (<i>Savelinus fontinalis</i>)	NOEC embryonic survival = 0.31 mg/L at pH 5.2 (fresh water) NOEC embryonic survival = 0.15 mg/L at pH 5.5 (fresh water) NOEC weight at 10 months = 0.13 mg/L at pH 5.5 (fresh water)

Mesocosm studies:

Fish (<i>Savelinus fontinalis</i>)	NOEC = 0.13 mg/L at pH 5.56 (fresh water)
Phytoplankton	NOEC = 0.13 mg/L at pH 5.6 (fresh water)
Lake-dwelling fish	NOEC = 0.0058 mg/L at pH 5.93 (fresh water)

PNEC (Predicted No-Effect Concentration): no PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a sulphuric acid spill, the change in pH of the water must be calculated or measured. **Variation by one pH unit can affect flora and fauna.** The average pH of water can vary in seawater from 8 to 8.4 (stable pH with high buffering capacity) and in fresh water from 6 to 7.5.

Examples of pH in natural waters

Brest's estuary	Fos sur Mer	Fresh water
8	7.95	6 - 7.5

ANNEX 3: FAX FORMAT DATA CARD

Sulphuric acid Sulfuric acid, oil of vitriol, vitriol, battery acid, chamber acid, fertilizer acid, mattling acid, electrolyte acid, dihydrogen sulphate.	H_2SO_4	CAS n°: 7664-93-9 EC N° (EINECS): 231-639-5 Index n°: 016-020-00-8 UN N°: 1830 Class: 8
---	-----------	---

First aid information

The corrosive action of sulphuric acid can appear after a certain delay: **it is important to take immediate action.**

Immediately remove all soiled or spotted clothes, including shoes.

Intoxication by inhalation: Move the victim into the open air and lie them down. Prop the person up to a half-sitting position. Apply artificial respiration if necessary. Transfer to hospital immediately.

Skin contact: Rinse with plenty of water at length while rapidly removing soiled clothes in the shower.

Finish cleaning with a neutralising solution (5 to 10 % triethanolamine solution). In the event of extensive burns, transfer to hospital immediately.

Eye contact: Immediately wash the eyes with plenty water for at least 15 minutes, keeping the eyelids open. Consult a specialist.

Intoxication by ingestion: Do not induce vomiting. Rinse the mouth and lips with water if the person is conscious. Transfer to hospital immediately.

Physical data

Relative density (water = 1): 1.84 to 20°C (93 to 100 %)

Vapour density (air = 1): 3.4

Solubility in fresh water: soluble in water at 20°C (with release of heat)

Vapour pressure/tension: < 0.001 hPa at 20°C

Olfactory threshold in air: > 0.25 ppm (= 1 mg/m³)

pH of the solution: very acidic < 1 (94 to 98 %)

pK_a: 1st pK_a value < 0
2nd pK_a value = 1.92

Viscosity at 25°C: 21 mPa.s

Freezing point: -15°C (94 to 96 %); -10°C / +5°C (97 %); +5°C (98 %)

Boiling point at 1 atm: 335°C (98 %); 290°C (92 %)



C: corrosive

R35: causes severe burns.

S26: in case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S30: never add water to this product.

S45: in case of accident or if you feel unwell, seek medical advice. Show the label where possible.

231-639-5: EC labelling.

Ecotoxicological data

• **Acute ecotoxicity:**

Crustacean (*Daphnia magna*) EC₅₀ (24h) = 29 mg/L (fresh water)

Fish (*Brachydanio rerio*) LC₅₀ (24h) = 82 mg/L (fresh water)

Fish (*Lepomis macrochirus*) LC₅₀ (48h) = 49 mg/L (fresh water)

Fish (*Pleuronectes platessa*) LC₅₀ (48h) = 100 to 330 mg/L (seawater)

• **Chronic ecotoxicity:**

Seaweed (*Gymnodium sp.*) NOEC at pH 5.6 = 0.13 mg/L

Insect (*Tanytarsus dissimilis*) NOEC (35 d) = 0.15 mg/L (fresh water)

Fish (*Jordanella floridae*) NOEC = 0.025 mg/L (fresh water)

Fish (*Savelinus fontinalis*) (fresh water)

NOEC embryonic survival = 0.31 mg/L at pH 5.2

NOEC embryonic survival = 0.15 mg/L at pH 5.5

NOEC weight at 10 months = 0.13 mg/L at pH 5.5

Mesocosm studies:

Fish (*Savelinus fontinalis*) NOEC = 0.13 mg/L at pH 5.56 (fresh water)

Phytoplankton NOEC = 0.13 mg/L at pH 5.6 (fresh water)

Lake-dwelling fish NOEC = 0.0058 mg/L at pH 5.93 (fresh water)

• **PNEC:** no PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a sulphuric acid spill, the change in pH of the water must be calculated or measured. **Variation by one pH unit can affect flora and fauna.** The average pH of water can vary in seawater from 8 to 8.4 (stable pH with high buffering capacity) and in fresh water from 6 to 7.5.

Toxicological data

Acute human toxicity

- By ingestion: burns to the mouth and digestive tract with laryngeal oedema, vomiting of blood, possible perforation of digestive tract and a state of shock.
- By skin contact: severe burns.
- By eye contact: redness, pain, oedema, corneal opaqueness and possible loss of sight.

If concentrated solutions of sulphuric acid come into contact with the skin or eyes, they cause local caustic lesions if the affected area is not rapidly decontaminated.

- By inhalation: exposure to vapours causes coughing, breathing difficulties and can lead to bronchial irritation and pulmonary oedema in the presence of high concentrations. The effects are influenced by several factors including the particle size, the concentration of the product and the degree of humidity. Physical exercise can exacerbate symptoms.

Asthmatics are more sensitive to the bronchoconstrictor effects of inhaled acid.

Chronic human toxicity

- Repeated exposure by inhalation: dental erosion and chronic bronchitis.
- Irritant contact dermatitis can arise in the case of repeated contact with sulphuric acid or its solutions.

- The ACGIH (notation A2) and IARC (group 1) believe that exposure to mists of strong inorganic acid containing sulphuric acid is carcinogenic for humans.

Persistence in the environment

The risk presented by sulphuric acid for the environment is due to hydronium ions (pH effect). The effect of sulphuric acid therefore depends on the buffering capacity of the aquatic or terrestrial ecosystem. A pH of less than 5.5 is harmful for aquatic life. The effect of this ion is naturally reduced by dilution and in seawater by a buffering effect.

- **Risk for the environment:** A high concentration of sulphuric acid in the water will increase the acidity of the water, which can be harmful for aquatic life. In seawater, some types of algae can survive at a pH of 6, but cannot endure a decrease in pH to less than 5.5. Fresh water fish cannot survive at a pH of less than 4.5. Marine organisms generally cannot endure significant variations in pH.
- **Breakdown:** sulphuric acid reacts rapidly with the ions present in the environment and transforms into salts.

- **Bioaccumulation:** sulphuric acid is a substance which does not bioaccumulate along the food chain.
- **Indirect pollution:** sulphuric acid is a strong acid which can lead to the release of the metal ions contained in the mud or sediments present at the base of the water column (case for lakes and ports).
- **Octanol/water partition coefficient:** N/A
- **Organic carbon/water partition coefficient:** N/A
- **Bioconcentration factor (BCF):** N/A
- **MARPOL classification:** C until 31/12/2006
Y from 01/01/2007
- **SEBC classification:** D

Particular risks

- **Danger:**
 - Heating the receptacle can cause an increase in pressure and the receptacle may shatter.
 - In the presence of heat, sulphuric acid breaks down into sulphur oxides and water.
 - Possibility of attacking metals, in the presence of heat or humidity, and production of hydrogen which may form an explosive mixture with the air.Vapours are invisible and heavier than air. They spread out across the ground and can infiltrate drains and underground systems.

- **Stability and reactivity**
 - Keep away from heat.
 - Substances to be avoided: metals (in the presence of heat or humidity), propargyl alcohol (explosive reaction), water, bases (exothermic reaction), combustible matters (carbonisation) and oxidants.
 - Hygroscopic substance: it absorbs water from damp air.
 - Dangerous products of decomposition: formation of (flammable and explosive) hydrogen by corrosion of metals.

Transportation	Handling	Use
<p>General data: Class: 8 Corrosive liquid Labels: 8 Identification n° (UN): 1830 Land transportation RID/ADR Hazard classification: 80 Packaging group: II Classification code: C1 Transportation via inland waterways ADN/ADNR Hazard classification: 80 Classification code: C1 Maritime and air transportation IMDG/IATA Packaging group: II Marine pollutant: no</p>	<p>In high concentrations of vapours:</p> <ul style="list-style-type: none"> - Ventilate and evacuate appropriately. - Provide showers and eye washers. - Ensure that there is a water source nearby. - Ensure that SCBA (Self-Contained Breathing Equipment) is available nearby. 	<ul style="list-style-type: none"> - Eliminate all sources of ignition at tank openings. Do not smoke. - Hot works permit for cutting and welding operations. - Do not add water to the acid. - Gradually put the acid into contact with the water (strong exothermic reaction). - Immediately remove pools of the product.

Storage	Incompatible substances	Recommended packaging materials
<ul style="list-style-type: none"> - Prevent all arrivals of water. - Keep away from heat. - Store outdoors. - Store in firmly closed receptacles in a cool and well aerated place. - Store in tanks equipped with dehydrating breathers. - Provide a retention tank and ensure that the ground is impermeable and resistant to corrosion, with a drainage system sending run-off to a neutralisation tank. - Ground the tanks and ensure that the electric equipment is watertight. 	<ul style="list-style-type: none"> - Propargyl alcohol (explosive reaction). - Water, bases, combustible substances, oxidants. 	<ul style="list-style-type: none"> - For small quantities: ordinary steel. - For large quantities: stainless steel (NSMC or NS 22S), carbon steel. - Packaging materials to be avoided: light metals and alloys in the damp conditions, including for parts in contact with the product.

October 2006

ANNEX 4: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Dangerous goods (IMO, 2002)

Regulations governing the carriage in bulk of hazardous liquid substances (MARPOL Annex II) provide valuable indications on the hazards that such substances can produce during transportation.

Noxious liquid substances are divided into 4 categories (A, B, C and D) starting with the most dangerous substances (MARPOL A) and ending with the least dangerous ones (MARPOL D).

The MARPOL classification system is based on risk assessment profiles for chemicals transported in bulk by sea, as defined by a GESAMP working group (Group of Experts on the Scientific Aspects of Marine Pollution).

Category A - Noxious liquid substances which, if discharged into the sea from tank washing or deballasting operations, are deemed to present a major hazard to marine resources or human health or can cause serious harm to amenities or other legitimate uses of the sea and therefore justify the implementation of strict pollution response measures.

Category B - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to present a hazard to marine resources or human health and can harm amenities or other legitimate uses of the sea and therefore justify the implementation of special pollution response measures.

Category C - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to be a minor risk for marine resources or human health or cause, to some extent, harm to amenities or other legitimate uses of the sea and therefore require special operating conditions.

Category D - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to be a noticeable risk for marine resources or human health or have a very slight effect on amenities or other legitimate uses of the sea and therefore require certain precautions concerning operating conditions.

ANNEXE 4b: NEW CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Revised MARPOL Annex II (IMO, 2005)

The revised Annex II Regulations for the control of pollution by noxious liquid substances in bulk was adopted in October 2004. It includes a new four-category categorization system for noxious and liquid substances. The revised annex entered into force on 1 January 2007.

The new categories are:

Category X: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a major hazard to either marine resources or human health and, therefore, justify the prohibition of the discharge into the marine environment;

Category Y: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment;

Category Z: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a minor hazard to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment; and

Other Substances: substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning or deballasting operations.

The revision of this annex is based on the modification of other classifications such as the GESAMP classification and led to consequential amendments to the IBC Code.