

SAFETY DATA SHEET

Based upon Regulation (EC) No 1907/2006, as amended by Regulation (EU) No 2020/878

sulfuric acid, conc=93-99.5%

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

| Product name | : sulfuric acid, conc=93-99.5% |
|---------------------------|---|
| Synonyms | : sulfuric-acid- |
| Registration number REACH | : 01-2119458838-20-0102 (Nyrstar Belgium NV/SA) |
| | 01-2119458838-20-0086 (Nyrstar Budel BV) |
| | 01-2119458838-20-0103 (Nyrstar France SAS) |
| Product type REACH | : Substance/mono-constituent |
| CAS number | : 7664-93-9 |
| EC index number | : 016-020-00-8 |
| EC number | : 231-639-5 |
| Molecular mass | : 98.08 g/mol |
| Formula | : H2SO4 |

1.2. Relevant identified uses of the substance or mixture and uses advised against

1.2.1 Relevant identified uses

IU01: Production of sulphuric acid (ES1)

IU02: Use of sulphuric acid as an intermediate in manufacture of inorganic and organic chemicals incl. fertilizers (ES2)

- IU03: Use of sulphuric acid as a processing aid, catalyst, dehydrating agent, pH regulator (ES3)
- IU04: Use of sulphuric acid for extractions and processing of minerals, ores (ES4)
- IU05: Use of sulphuric acid in the process of surface treatments, purification and etching (ES5)

IU06: Use of sulphuric acid in electrolytic processes (ES6)

IU07: Use of sulphuric acid in gas purification, scrubbing, flue gas scrubbing (ES7)

- IU08: Use of sulphuric acid in production of sulphuric acid contained batteries (ES8)
- IU09: Use of sulphuric acid in maintenance of sulphuric acid contained batteries (ES9)
- IU10: Use of sulphuric acid in recycling of sulphuric acid contained batteries (ES10)

IU11: Use of sulphuric acid contained batteries (ES11)

- IU12: Use of sulphuric acid as laboratory chemicals (ES12)
- IU13: Use of sulphuric acid in industrial cleaning (ES13)
- IU14: mixing, preparation and repackaging of sulphuric acid (ES14)

For more detailed information regarding the Identified Uses and the associated Exposure Scenarios: see attached annex

1.2.2 Uses advised against

No uses advised against known

1.3. Details of the supplier of the safety data sheet

Supplier of the safety data sheet

Nyrstar Belgium N.V. on behalf of Nyrstar Sales & Marketing A.G. 7inkstraat 1 B-2490 Balen +32 14 44 95 00 🛥 +32 14 81 05 31 infoSDS@nyrstar.com Nyrstar Budel B.V. on behalf of Nyrstar Sales & Marketing A.G. Hoofdstraat 1 6024 AA Budel-Dorplein +32 14 44 96 80 **4** + 32 14 44 95 52 infoSDS@nyrstar.com Nyrstar France S.A.S. on behalf of Nyrstar Sales & Marketing A.G. Rue Jean Jacques Rousseau F-59950 Auby 2 +32 14 44 96 80 🛥 +33 3 27 88 39 48 infoSDS@nyrstar.com

Manufacturer of the product

Nyrstar Sales & Marketing SA 1 Rue de Jargonnant CH-1207 Geneva infoSDS@nyrstar.com

1.4. Emergency telephone number

Created by: Brandweerinformatiecentrum voor gevaarlijke stoffen vzw (BIG) Technische Schoolstraat 43 A, B-2440 Geel http://www.big.be © BIG vzw Reason for revision: 4;8;9;11;12 Revision number: 0200

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878-

24h/24h (Telephone advice: English, French, German, Dutch) :

+32 14 58 45 45 (BIG)

SECTION 2: Hazards identification

2.1. Classification of the substance or mixture

| Classified as dangerous according to the criteria of Regulation (EC) No 1272/2008 | | | | | |
|---|-------------|--|--|--|--|
| Class | Category | Hazard statements | | | |
| Skin Corr. | category 1A | H314: Causes severe skin burns and eye damage. | | | |
| Eye Dam. | category 1 | H318: Causes serious eye damage. | | | |

2.2. Label elements

| Signal word | Danger |
|--------------------|--|
| H-statements | |
| H314 | Causes severe skin burns and eye damage. |
| P-statements | |
| P280 | Wear protective gloves, protective clothing and eye protection/face protection. |
| P260 | Do not breathe vapours/mist. |
| P304 + P340 | IF INHALED: Remove person to fresh air and keep comfortable for breathing. |
| P303 + P361 + P352 | IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse simultaneously with neutralizing agent Diphoterine or equivalent neutralizing agent. Use complete bottle. Rinse under emergency shower for 1 to 2 minutes and continue rinsing under regular shower for 10 minutes with water at 35-36°C |
| P305 + P351 | IF IN EYES: Rinse cautiously with neutralization agent Diphoterine or equivalent neutralizing agent for several minutes and continue rinsing with water for 10 minutes. |
| P310 | Immediately call a POISON CENTER/doctor. |

2.3. Other hazards

The criteria of PBT and vPvB as listed in Annex XIII of Regulation (EC) No 1907/2006 do not apply to inorganic substances Strong inorganic acid mists containing sulfuric acid are carcinogenic to humans

SECTION 3: Composition/information on ingredients

3.1. Substances

| | | | | | - | |
|------------------------------|-----------|-----------|---------------------------------|------------|------------------|---------------|
| Name | CAS No | Conc. (C) | Classification according to CLP | Note | Remark | M-factors and |
| REACH Registration No | EC No | | | | | ATE |
| sulfuric acid, conc=93-99.5% | 7664-93-9 | 93%<=C | Skin Corr. 1A; H314 | (1)(2)(10) | Mono-constituent | |
| 01-2119458838-20 | 231-639-5 | <=99.5% | Eye Dam. 1; H318 | | | |
| | | | Skin Corr. 1A; H314: C≥15%, | | | |
| | | | (CLP Annex VI (ATP 0)) | | | |
| | | | Skin Irrit. 2; H315: 5%≤C<15% | | | |
| | | | , (CLP Annex VI (ATP 0)) | | | |
| | | | Eye Irrit. 2; H319: 5%≤C<15%, | | | |
| | | | (CLP Annex VI (ATP 0)) | | | |

(1) For H- and EUH-statements in full: see section 16

(2) Substance with a Community workplace exposure limit

(10) Subject to restrictions of Annex XVII of Regulation (EC) No. 1907/2006

3.2. Mixtures

Not applicable

SECTION 4: First aid measures

4.1. Description of first aid measures

General:

Observe (own) safety. If possible, approach victim and check vital functions. In case of injury and/or intoxication, call the European emergency number 112. Treat symptoms starting with most life-threatening injuries and disorders. Keep victim under observation, possibility of delayed symptoms.

After inhalation:

Remove victim into fresh air. Immediately consult a doctor/medical service.

After skin contact:

Take off immediately all contaminated clothing and simultaneously rinse with neutralizing agent (BUMB, Diphoterine or equivalent neutralizing agent). Use complete bottle. Continue rinsing under emergency shower for 1 to 2 minutes and continue rinsing under regular shower for 10 minutes with water at 35-36°C. Cut clothing; never remove burnt clothing from the wound. Do not give any pain medication. Consult a doctor/medical service.

After eye contact:

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Rinse cautiously with neutralization agent (BUMB, Diphoterine or equivalent neutralizing agent) for several minutes and continue rinsing with plenty of water during 10 minutes. Consult a doctor/medical service.

After ingestion:

Rinse mouth with water. Immediately after ingestion: give small amount of water to drink. Immediately consult a doctor/medical service. Do not wait for symptoms to occur to consult Poison Center.

4.2. Most important symptoms and effects, both acute and delayed

4.2.1 Acute symptoms

After inhalation:

Dry/sore throat. Coughing. Irritation of the respiratory tract. Irritation of the nasal mucous membranes. ON CONTINUOUS EXPOSURE/CONTACT: Corrosion of the upper respiratory tract. FOLLOWING SYMPTOMS MAY APPEAR LATER: Possible laryngeal spasm/oedema. Risk of pneumonia. Risk of lung oedema. Respiratory difficulties.

After skin contact: Caustic burns/corrosion of the skin.

After eve contact:

Corrosion of the eye tissue. Permanent eye damage.

After ingestion:

Nausea. Abdominal pain. Blood in stool. Blood in vomit. Burns to the gastric/intestinal mucosa. AFTER INGESTION OF HIGH QUANTITIES: Shock. **4.2.2 Delayed symptoms**

No effects known.

4.3. Indication of any immediate medical attention and special treatment needed

If applicable and available it will be listed below.

SECTION 5: Firefighting measures

5.1. Extinguishing media

5.1.1 Suitable extinguishing media:

Small fire: Quick-acting ABC powder extinguisher, Quick-acting BC powder extinguisher, Quick-acting CO2 extinguisher. Major fire: Class B foam (alcohol-resistant); after consulting specialist.

5.1.2 Unsuitable extinguishing media:

Small fire: Water (quick-acting extinguisher, reel); risk of puddle expansion, Quick-acting class B foam extinguisher. Major fire: Water.

5.2. Special hazards arising from the substance or mixture

On burning: release of toxic and corrosive gases/vapours (sulphur oxides). Violent exothermic reaction with water (moisture): release of corrosive gases/vapours.

5.3. Advice for firefighters

5.3.1 Instructions:

Cool tanks/drums with water spray/remove them into safety. When cooling/extinguishing: no water in the substance. Dilute toxic gases with water spray. Take account of toxic/corrosive precipitation water. Heat exposure: dilute toxic gas/vapour with water spray.

5.3.2 Special protective equipment for fire-fighters:

Gloves (EN 374). Face shield (EN 166). Corrosion-proof suit (EN 14605). Large spills/in enclosed spaces: self-contained breathing apparatus (EN 136 + EN 137). Large spills/in enclosed spaces: gas-tight suit (EN 943). Heat/fire exposure: self-contained breathing apparatus (EN 136 + EN 137).

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

No naked flames. Keep containers closed. Avoid ingress of water in the containers. Large spills/in confined spaces: consider evacuation. 6.1.1 Protective equipment for non-emergency personnel

See section 8.2

6.1.2 Protective equipment for emergency responders

Gloves (EN 374). Face shield (EN 166). Corrosion-proof suit (EN 14605). Large spills/in enclosed spaces: self-contained breathing apparatus (EN 136 + EN 137). Large spills/in enclosed spaces: gas-tight suit (EN 943).

Suitable protective clothing See section 8.2

6.2. Environmental precautions

Contain released product, collect/pump into suitable containers. Plug the leak, cut off the supply. Dam up the liquid spill. Prevent soil and water pollution. Prevent spreading in sewers.

6.3. Methods and material for containment and cleaning up

Neutralize spill with lime, sodium bicarbonate, soda (sodium carbonate) or soda ash. Neutralized substance: shovel into closing drums. Carefully collect the spill/leftovers. Damaged/cooled tanks must be emptied. Clean contaminated surfaces with an excess of water. Take collected spill to manufacturer/competent authority. Wash clothing and equipment after handling.

6.4. Reference to other sections

See section 13.

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SECTION 7: Handling and storage

The information in this section is a general description. If applicable and available, exposure scenarios are attached in annex. Always use the relevant exposure scenarios that correspond to your identified use.

7.1. Precautions for safe handling

Keep away from naked flames/heat. Gas/vapour heavier than air at 20°C. Observe very strict hygiene - avoid contact. Remove contaminated clothing immediately. Do not discharge the waste into the drain. Never add water to this product. Never dilute by pouring water to the acid. Always add the acid to the water. Keep container tightly closed.

7.2. Conditions for safe storage, including any incompatibilities

7.2.1 Safe storage requirements:

Store in a dry area. Keep container in a well-ventilated place. Keep locked up. Protect against frost. Store at ambient temperature. Provide for a tub to collect spills. Unauthorized persons are not admitted. Under a shelter/in the open. Aboveground. Keep only in the original container. Store only in a limited quantity. Meet the legal requirements.

7.2.2 Keep away from:

Heat sources, combustible materials, reducing agents, (strong) bases, metals, cellulosic materials, organic materials, oxidizing agents, alcohols, amines, water/moisture.

7.2.3 Suitable packaging material:

Carbon steel, polyethylene, polypropylene, glass, stoneware/porcelain.

7.2.4 Non suitable packaging material:

Monel steel, lead, aluminium, iron, copper, zinc, nickel, bronze.

7.3. Specific end use(s)

If applicable and available, exposure scenarios are attached in annex. See information supplied by the manufacturer.

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

FII

8.1.1 Occupational exposure

a) Occupational exposure limit values

If limit values are applicable and available these will be listed below.

| EU | | |
|--------------------------|--|------------------------|
| | Time-weighted average exposure limit 8 h (Indicative occupational exposure limit value) | 0.5 ppm |
| | Time-weighted average exposure limit 8 h (Indicative occupational exposure limit value) | 1.3 mg/m³ |
| | · · · · | 1 ppm |
| | | 2.7 mg/m ³ |
| Sulphuric acid (mist) | | 0.05 mg/m ³ |
| Belgium | | |
| Acide sulfurique (brume) | Time-weighted average exposure limit 8 h | 0.2 mg/m ³ |
| Soufre (dioxyde de) | Time-weighted average exposure limit 8 h | 0.5 ppm |
| - | Time-weighted average exposure limit 8 h | 1.3 mg/m ³ |
| | | 1 ppm |
| | Short time value | 2.7 mg/m ³ |
| The Netherlands | | |
| | Time-weighted average exposure limit 8 h (Public occupational exposure limit value) | 0.7 mg/m ³ |
| (| Short time value (Public occupational exposure limit value) | 0.7 mg/m ³ |
| | Time-weighted average exposure limit 8 h (Public occupational exposure limit value) | 0.012 ppm |
| | Time-weighted average exposure limit 8 h (Public occupational exposure limit value) | 0.05 mg/m ³ |
| France | | |
| | Time-weighted average exposure limit 8 h (VRI: Valeur réglementaire indicative) | 0.05 mg/m³ |
| | Short time value (VL: Valeur non réglementaire indicative) | 3 mg/m³ |
| | Time-weighted average exposure limit 8 h (VRI: Valeur réglementaire indicative) | 0.5 ppm |
| | Time-weighted average exposure limit 8 h (VRI: Valeur réglementaire indicative) | 1.3 mg/m ³ |
| | • | 1 ppm |
| | Short time value (VRI: Valeur réglementaire indicative) | 2.7 mg/m ³ |
| Germany | | |
| | Time-weighted average exposure limit 8 h (TRGS 900) | 1 ppm |
| | | |
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| Schwefeldioxid | Time-weighted average exposure limit 8 h (TRGS 900) | 2.7 mg/m ³ |
|------------------------------------|--|------------------------|
| Schwefelsäure | Time-weighted average exposure limit 8 h (TRGS 900) | 0.1 mg/m ³ |
| Austria | | • |
| Schwefelsäure | Tagesmittelwert (MAK) | 0.1 mg/m ³ |
| | Kurzzeitwert Mow 8x (MAK) | 0.2 mg/m ³ |
| | | |
| UK Sulphuric acid (mist) | Time-weighted average exposure limit 8 h (Workplace exposure limit (EH40/2005)) | 0.05 mg/m ³ |
| | | 0.05 mg/m ³ |
| Sulphuric acid (mist) | | 0.05 mg/m ³ |

b) National biological limit values

If limit values are applicable and available these will be listed below.

8.1.2 Sampling methods

| Product name | Test | Number |
|---|-------|----------|
| NON-VOLATILE ACIDS (Sulfuric Acid) | NIOSH | 7908 |
| Sulfur Dioxide (organic and inorganic gases by Extractive FTIR) | NIOSH | 3800 |
| Sulfur Dioxide | NIOSH | 6004 |
| Sulfur Dioxide | OSHA | 1011 |
| Sulfur Dioxide | OSHA | ID 104 |
| Sulfur Dioxide | OSHA | ID 200 |
| Sulfuric Acid | NIOSH | 7903 |
| Sulfuric Acid | OSHA | ID 113 |
| Sulfuric Acid | OSHA | ID 165SG |

8.1.3 Applicable limit values when using the substance or mixture as intended

If limit values are applicable and available these will be listed below.

8.1.4 Threshold values

E

DNEL/DMEL - Workers sulfuric acid, conc=93-99.5%

| Effect level (DNEL/DMEL) | Туре | Value | Remark |
|--------------------------|------------------------------------|------------------------|--------|
| DNEL | Long-term local effects inhalation | 0.05 mg/m ³ | |
| | Acute local effects inhalation | 0.1 mg/m³ | |
| | Long-term local effects inhalation | 1.3 mg/m ³ | SO2 |
| | Acute local effects inhalation | 2.7 mg/m ³ | SO2 |

DNEL/DMEL - General population

| Effect level (DNEL/DMEL) | Туре | Value | Remark |
|--------------------------|------------------------------------|------------|--------|
| DNEL | Long-term local effects inhalation | 0.53 mg/m³ | SO2 |

8.1.5 Control banding

If applicable and available it will be listed below.

8.2. Exposure controls

The information in this section is a general description. If applicable and available, exposure scenarios are attached in annex. Always use the relevant exposure scenarios that correspond to your identified use.

8.2.1 Appropriate engineering controls

Keep away from naked flames/heat. Measure the concentration in the air regularly. Carry operations in the open/under local exhaust/ventilation or with respiratory protection.

8.2.2 Individual protection measures, such as personal protective equipment

Observe very strict hygiene - avoid contact. Do not eat, drink or smoke during work.

a) Respiratory protection:

Full face mask with filter type E, at concentrations in air higher than the exposure limit for sulfur dioxide (SO2). Dust/aerosol mask with filter type P3 at concentrations in air higher than the exposure limit for sulfuric acid (H2SO4).

b) Hand protection:

Protective gloves against chemicals (EN 374).

| Materials | Measured breakthrough time | Thickness | Protection index | Remark |
|----------------------------------|-------------------------------|-----------|------------------|-----------------|
| butyl rubber | > 120 minutes | 0.5 mm | Class 4 | |
| viton | > 480 minutes | 0.4 mm | Class 6 | |
| natural rubber | | | | Poor resistance |
| nitrile rubber | | | | Poor resistance |
| neoprene (chloroprene rubber) | | | | Poor resistance |
| leather | | | | Poor resistance |

c) Eye protection:

Face shield (EN 166). Protective goggles (EN 166).

d) Skin protection:

Corrosion-proof clothing (EN 14605).

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8.2.3 Environmental exposure controls:

See sections 6.2, 6.3 and 13

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

| Physical form | Liquid | | | |
|---------------------------|--|--|--|--|
| Viscosity | Oily | | | |
| Odour | Odourless | | | |
| Odour threshold | No data available in the literature | | | |
| Colour | Colourless to brown | | | |
| Translucency | Clear | | | |
| Particle size | Not applicable (liquid) | | | |
| Explosion limits | Not applicable | | | |
| Flammability | Not classified as flammable | | | |
| Log Kow | Not relevant | | | |
| Dynamic viscosity | 22.5 mPa.s ; 20 °C ; 95 % | | | |
| | 15 mPa.s ; 20 °C ; 75 % | | | |
| Kinematic viscosity | No data available in the literature | | | |
| Melting point | 10 °C ; 100 % ; Equivalent to OECD 102 | | | |
| | 3 °C ; 98 % ; Equivalent to OECD 102 | | | |
| Boiling point | 190 °C ; 98 % ; Equivalent to EU Method A.2 | | | |
| | 330 °C ; 96 % ; Equivalent to EU Method A.2 | | | |
| Relative vapour density | No data available in the literature | | | |
| Vapour pressure | 0.49 hPa ; 20 °C ; 75 % ; Equivalent to OECD 104 | | | |
| | 2.14 hPa ; 20 °C ; 65 % ; Equivalent to EU Method A.4 | | | |
| | 0.06 hPa ; 20 °C ; 90 % ; Equivalent to EU Method A.4 | | | |
| Solubility | Water ; miscible ; EU Method A.6 | | | |
| Relative density | 1.84 ; 20 °C ; 93 % - 100 % ; Equivalent to OECD 109 | | | |
| Absolute density | 1840 kg/m ³ ; 20 °C ; Equivalent to OECD 109 ; 93 % - 100 % | | | |
| Decomposition temperature | No data available in the literature | | | |
| Auto-ignition temperature | Not applicable | | | |
| Flash point | Not applicable | | | |
| рН | No data available in the literature | | | |

9.2. Other information

No data available

SECTION 10: Stability and reactivity

10.1. Reactivity

Acid reaction.

10.2. Chemical stability

Unstable on exposure to moisture.

10.3. Possibility of hazardous reactions

Violent exothermic reaction with water (moisture): release of corrosive gases/vapours. Reacts with many compounds: (increased) risk of fire/explosion. Reacts exothermically with organic material: risk of spontaneous ignition. Reacts violently with combustible materials: (increased) risk of fire/explosion. Reacts violently with (some) bases: heat release resulting in increased fire or explosion risk. Reacts with (strong) reducers: (increased) risk of fire/explosion.

10.4. Conditions to avoid

Precautionary measures

Keep away from naked flames/heat.

10.5. Incompatible materials

Combustible materials, reducing agents, (strong) bases, metals, cellulosic materials, organic materials, oxidizing agents, alcohols, amines, water/moisture.

10.6. Hazardous decomposition products

Aqueous solution reacts with (some) metals: release of highly flammable gases/vapours (hydrogen). On burning: release of toxic and corrosive gases/vapours (sulphur oxides).

SECTION 11: Toxicological information

11.1. Information on hazard classes as defined in Regulation (EC) No 1272/2008

11.1.1 Test results

Reason for revision: 4;8;9;11;12

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- Toxicokinetics: summary

Basic toxicokinetics: The effects of sulphuric acid are essentially the result of the hydrogen ion (local deposition of H+, pH change) rather than an effect of the sulphate ion. Sulphuric acid (as such) is not expected to be absorbed or distributed throughout the body as the acid will rapidly dissociate; the hydrogen ion will form water. The sulphate anion will enter the body electrolyte pool, its kinetics will be governed by sulphate homeostatic mechanisms, and is therefore not predicted play a specific toxicological role. This supposition is supported by experiments which have studied the active component in inorganic acids on various endpoints, using different acids or salts. The results of these studies lead to the conclusion that the observed effects are due to the hydrogen ion, while the anion appeared to have no effect.

In a study of the clearance of radiolabeled sulphuric acid aerosol in different species, the authors observed that the sulphur from sulphuric acid was rapidly cleared (from 2 -9 minutes) from the lungs of animals into the blood following inhalation exposure (Dahl, 1983). Sulphate is a normal constituent of the blood (present at 0.8 -1.2 mg/dl) and is a normal metabolite of sulphur-containing amino acids. The body has efficient sulphate homeostatic mechanisms and excess sulphate is excreted in the urine (capacity-limited proximal tubular absorption); urinary sulphate concentrations of up to 500 umol/dl/kg bw have been reported. The body pool of this anion is large, and it is therefore unlikely that occupational exposure will significantly add to the normal body burden. Systemic absorption of the hydrogen ion following dermal or inhalation exposure to sulphuric acid is not predicted to be significant, and the low level of hydrogen ions absorbed will be effectively controlled by the homeostatic mechanisms governing pH including the action of the enzyme carbonic anhydrase and NA+/H+ exchange in the proximal renal tubule. Although acidaemia and metabolic acidosis have been noted following cases of ingestion exposure (which will be much lower and effectively limited by respiratory tract irritation) or following dermal exposure (due to low dermal absorption and local dermal irritation).

The deposition of sulphuric particles in the human lung has been studied extensively. Deposition is influenced by subject age, particle size and breathing rate. Sulphuric acid particles are hygroscopic and therefore will absorb moisture present in the airways, thereby increasing particle size and potentially increasing particle retention. Respiratory mucus has a limited buffering capacity and may reduce tissue contact.

The absence of systemic effects in the large number of toxicity studies performed with sulphuric acid is consistent with this assessment of its toxicokinetics. The following information is taken into account for any hazard / risk assessment: Primary information is limited to a study of the absorption and kinetics of radiolabelled sulphate following the inhalation of sulphuric acid aerosols. Sulphuric acid immediately dissociates to the hydrogen and sulphate ions, with the hydrogen ion being responsible for the local toxicity (irritation and corrosivity) of sulphuric acid.

Dermal absorption: No dermal absorption is predicted under normal conditions of use, based on the physicochemical properties of the substance. However dermal absorption may occur when the integrity of the skin is lost (i. e. in accidental exposures resulting in burns).

The following information is taken into account for any hazard / risk assessment: No studies are proposed for scientific reasons and (given the corrosive nature of the substance), also reasons of animal welfare. No dermal absorption is predicted under normal conditions of use, based on the physicochemical properties of the substance.

Acute toxicity

sulfuric acid, conc=93-99.5%

| Route of exposure | Parameter | Method | Value | Exposure time | Species | Value | Remark |
|----------------------|-----------|--------------------|---------------|---------------|-------------|--------------------|--------|
| | | | | | | determination | |
| Oral | LD50 | Equivalent to OECD | 2140 mg/kg | | Rat (male / | Experimental value | |
| | | 401 | | | female) | | |
| Dermal | | | | | | Data waiving | |
| Inhalation (aerosol) | LC50 | Equivalent to OECD | 0.38 mg/l air | | Rat (male / | Experimental value | |
| , , | | 403 | 0. | | female) | | |

Conclusion

Not classified for acute toxicity

Corrosion/irritation

sulfuric acid, conc=93-99.5%

| Route of exposure | Result | Method | Exposure time | Time point | Species | Value | Remark |
|-------------------|--------------------------------------|--------|---------------|------------|---------|---------------|--------|
| | | | | | | determination | |
| Eye | Serious eye damage; category 1 | | | | | Annex VI | |
| Skin | Highly corrosive; category 1A | | | | | Annex VI | |

Conclusion

Causes severe skin burns and eye damage.

Not classified as irritating to the respiratory system

Respiratory or skin sensitisation

sulfuric acid, conc=93-99.5%

| R | oute of exposure | Result | Method | • | Observation time point | Species | Value determination | Remark |
|---|------------------|--------|--------|---|---------------------------|---------|---------------------|--------|
| 5 | Skin | | | | | | Data waiving | |
| Γ | nhalation | | | | | | Data waiving | |

Conclusion

Not classified as sensitizing for skin

Not classified as sensitizing for inhalation

Specific target organ toxicity

sulfuric acid, conc=93-99.5%

| Route of exposure | Parameter | Method | Value | Organ | Effect | Exposure time | Species | Value determination |
|-------------------|-----------|--------|-------|-------|--------|---------------|---------|---------------------|
| Oral | | | | | | | | Data waiving |
| Dermal | | | | | | | | Data waiving |

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| | | SU | Ifuri | c acid, co | onc=93- | ·99.5% | | |
|---|---|------------------------|-----------------|--|---|--------------------------------------|--------------------------|--------------------|
| Inhalation (aerosol) | LOAEC | OECD 412 | 0.3 mg/n air | n ³ Respiratory tract | | 4 weeks (6h / day, 5 days / week) | Rat (female) | Experimental value |
| Inhalation | | Human observation | > 1 mg/n air | n ³ Lungs | Lung tissue affection/dege neration | | Human | Weight of evidence |
| Conclusion Not classified for su | bchronic to: | xicity | · | | | | | |
| utagenicity (in vitro) ulfuric acid, conc=93-9 | 9.5% | | | | | | | |
| Result | Met | thod | Te | st substrate | Effect | Valu | e determination | Remark |
| Negative with meta activation, negative without metabolic activation | | Equivalent to OECD 471 | | acteria (S.typhimuriur | m) No effect | | rimental value | |
| Negative with meta activation, negative without metabolic activation | | EU Method B.10 | | ninese hamster lung problasts (V79) | | Expe | rimental value | |
| Negative with meta activation, negative without metabolic activation | | CD 476 | | ouse (lymphoma L51 ills) | 178Y | Expe | rimental value | |
| | | | | | | | | |
| utagenicity (in vivo) ulfuric acid, conc=93-9 | 9.5% | | | | | | | |
| 0 / / | 9.5% | Method | | Exposure time | Test substra | te Organ | v | alue determination |
| ulfuric acid, conc=93-9 | 9.5% | Method | | Exposure time | Test substra | te Organ | | alue determination |
| ulfuric acid, conc=93-9 Result Conclusion Not classified for m rcinogenicity | utagenic or | | ty | Exposure time | Test substra | te Organ | | |
| Ifuric acid, conc=93-9 Result Conclusion Not classified for m cinogenicity Ifuric acid, conc=93-9 | utagenic or 9.5% | genotoxic toxici | ty Value | Exposure time Exposure time | | te Organ | | |
| Ifuric acid, conc=93-9 Result Conclusion Not classified for m cinogenicity Ifuric acid, conc=93-9 Route of exposure Parat | utagenic or <u>9.5%</u> meter M e level Ca | genotoxic toxici | | Exposure time | | Effect | D Organ Ie Stomach | ata waiving |

Not classified for carcinogenicity

Reproductive toxicity

sulfuric acid, conc=93-99.5%

| | Parameter | Method | Value | Exposure time | Species | Effect | Value determination |
|--|-----------|---------------------------|-------------------------------|-------------------------------|------------------------|-----------|----------------------------|
| Developmental toxicity (Inhalation (aerosol)) | NOAEC | Equivalent to OECD 414 | 19.3 mg/m ³ air | 10 days (7h / day) | Mouse | No effect | Experimental value |
| Maternal toxicity (Inhalation (aerosol)) | NOAEC | Equivalent to OECD 414 | 5.7 mg/m³ air | 10 days (gestation, daily) | Mouse | No effect | Experimental value |
| Effects on fertility (Oral (stomach tube)) | NOEL | OECD 421 | 1000 mg/kg bw/day | 4 week(s) - 7 week(s) | Rat (male / female) | No effect | Experimental value |

Conclusion

Not classified for reprotoxic or developmental toxicity

Toxicity other effects

sulfuric acid, conc=93-99.5% No (test)data available

Chronic effects from short and long-term exposure

sulfuric acid, conc=93-99.5%

Red skin. Dry skin. Itching. Skin rash/inflammation. Affection/discolouration of the teeth. Inflammation/damage of the eye tissue.

11.2. Information on other hazards

No evidence of endocrine disrupting properties

Reason for revision: 4;8;9;11;12

Publication date: 2001-12-29 Date of revision: 2022-06-08

SECTION 12: Ecological information

12.1. Toxicity

sulfuric acid, conc=93-99.5%

| | Parameter | Method | Value | Duration | Species | Test design | Fresh/salt water | Value determination |
|---|-----------|----------|----------------------|-----------|----------------------------|------------------|---------------------|---|
| Acute toxicity fishes | LC50 | | 16 mg/l - 28 mg/l | 96 h | Lepomis macrochirus | Static system | Fresh water | Experimental value; Nominal concentration |
| Acute toxicity crustacea | EC50 | OECD 202 | > 100 mg/l | 48 h | Daphnia magna | Static system | Fresh water | Experimental value; GLP |
| Toxicity algae and other aquatic plants | ErC50 | OECD 201 | > 100 mg/l | 72 h | Desmodesmus subspicatus | Static system | Fresh water | Experimental value; Nominal concentration |
| Toxicity aquatic micro- organisms | NOEC | | 26 g/l | 37 day(s) | Activated sludge | Static system | Fresh water | Weight of evidence; Nominal concentration |

Conclusion

Not classified as dangerous for the environment according to the criteria of Regulation (EC) No 1272/2008

12.2. Persistence and degradability

Water

Log Kow

Biodegradability: not applicable

12.3. Bioaccumulative potential

sulfuric acid, conc=93-99.5%

| Method | Remark | Value | Temperature | Value determination |
|--------|--------|-------|-------------|---------------------|
| | | | | Not relevant |

Conclusion

Not bioaccumulative

12.4. Mobility in soil

No (test)data on mobility of the substance available

12.5. Results of PBT and vPvB assessment

The criteria of PBT and vPvB as listed in Annex XIII of Regulation (EC) No 1907/2006 do not apply to inorganic substances.

12.6. Endocrine disrupting properties

No evidence of endocrine disrupting properties

12.7. Other adverse effects

sulfuric acid, conc=93-99.5%

Greenhouse gases Not included in the list of fluorinated greenhouse gases (Regulation (EU) No 517/2014) Ozone-depleting potential (ODP) Not classified as dangerous for the ozone layer (Regulation (EC) No 1005/2009) Groundwater Groundwater pollutant Water ecotoxicity pH pH shift

SECTION 13: Disposal considerations

The information in this section is a general description. If applicable and available, exposure scenarios are attached in annex. Always use the relevant exposure scenarios that correspond to your identified use.

13.1. Waste treatment methods

13.1.1 Provisions relating to waste

European Union

Hazardous waste according to Directive 2008/98/EC, as amended by Regulation (EU) No 1357/2014 and Regulation (EU) No 2017/997. Waste material code (Directive 2008/98/EC, Decision 2000/0532/EC).

06 01 01* (wastes from the manufacture, formulation, supply and use (MFSU) of acids: sulphuric acid and sulphurous acid). Depending on branch of industry and production process, also other waste codes may be applicable.

13.1.2 Disposal methods

Reason for revision: 4;8;9;11;12

Publication date: 2001-12-29 Date of revision: 2022-06-08

Remove waste in accordance with local and/or national regulations. Hazardous waste shall not be mixed together with other waste. Different types of hazardous waste shall not be mixed together if this may entail a risk of pollution or create problems for the further management of the waste. Hazardous waste shall be managed responsibly. All entities that store, transport or handle hazardous waste shall take the necessary measures to prevent risks of pollution or damage to people or animals. Do not discharge into drains or the environment. Dispose of at authorized waste collection point.

13.1.3 Packaging/Container

European Union

Waste material code packaging (Directive 2008/98/EC).

15 01 10* (packaging containing residues of or contaminated by dangerous substances).

SECTION 14: Transport information

Road (ADR)

| 14. <u>1. UN number</u> | |
|--|--|
| UN number | 1830 |
| 14.2. UN proper shipping name | |
| Proper shipping name | sulphuric acid |
| 14.3. Transport hazard class(es) | |
| Hazard identification number | 80 |
| Class | 8 |
| Classification code | C1 |
| 14.4. Packing group | |
| Packing group | Ш |
| Labels | 8 |
| 14.5. Environmental hazards | |
| Environmentally hazardous substance mark | no |
| 14.6. Special precautions for user | |
| Special provisions | |
| Limited quantities | Combination packagings: not more than 1 liter per inner packaging for liquids. A package shall not weigh more than 30 kg. (gross mass) |

Rail (RID)

| 14. <u>1. UN number</u> | |
|--|---|
| UN number | 1830 |
| 14.2. UN proper shipping name | |
| Proper shipping name | sulphuric acid |
| 14.3. Transport hazard class(es) | |
| Hazard identification number | 80 |
| Class | 8 |
| Classification code | C1 |
| 14. <u>4. Packing group</u> | |
| Packing group | 11 |
| Labels | 8 |
| 14.5. Environmental hazards | |
| Environmentally hazardous substance mark | no |
| 14.6. Special precautions for user | |
| Special provisions | |
| Limited quantities | Combination packagings: not more than 1 liter per inner packaging for liquids. A package shall not weigh more than 30 kg. (gross mass) |

Inland waterways (ADN)

| 14. <u>1. UN number</u> | |
|--|---|
| UN number | 1830 |
| 14.2. UN proper shipping name | |
| Proper shipping name | sulphuric acid |
| 14.3. Transport hazard class(es) | |
| Class | 8 |
| Classification code | C1 |
| 14.4. Packing group | |
| Packing group | II |
| Labels | 8 |
| 14. <u>5. Environmental hazards</u> | |
| Environmentally hazardous substance mark | no |
| 14.6. Special precautions for user | |
| Special provisions | |
| Limited quantities | Combination packagings: not more than 1 liter per inner packaging for |
| | liquids. A package shall not weigh more than 30 kg. (gross mass) |

Sea (IMDG/IMSBC)

| 14.1. UN number | |
|----------------------------------|------------------------------|
| UN number | 1830 |
| 14.2. UN proper shipping name | |
| Reason for revision: 4;8;9;11;12 | Publication date: 2001-12-29 |
| | Date of revision: 2022-06-08 |
| | |

| Proper shipping name | sulphuric acid |
|--|---|
| 14.3. Transport hazard class(es) | |
| Class | 8 |
| 14.4. Packing group | |
| Packing group | II |
| Labels | 8 |
| 14.5. Environmental hazards | |
| Marine pollutant | - |
| Environmentally hazardous substance mark | no |
| 14.6. Special precautions for user | |
| Special provisions | |
| Limited quantities | Combination packagings: not more than 1 liter per inner packaging for |
| | liquids. A package shall not weigh more than 30 kg. (gross mass) |
| 14.7. Maritime transport in bulk according to IMO inst | ruments |
| Annex II of MARPOL 73/78 | Not applicable, based on available data |
| r (ICAO-TI/IATA-DGR) | |
| • • • | |
| 14.1. UN number | 1830 |
| 14.2. UN proper shipping name | 1050 |
| Proper shipping name | sulphuric acid |
| 14.3. Transport hazard class(es) | |
| Class | 8 |
| 14.4. Packing group | 0 |
| Packing group | 11 |
| Labels | 8 |
| 14.5. Environmental hazards | |
| Environmentally hazardous substance mark | no |
| 14.6. Special precautions for user | טוע |
| Special provisions | |
| Passenger and cargo transport | |
| Limited quantities: maximum net quantity per pac | kaging 0.5 L |
| Enniced quantities. maximum net quantity per pac | |

SECTION 15: Regulatory information

15.1. Safety, health and environmental regulations/legislation specific for the substance or mixture

European legislation: Explosives precursors

Acquisition, introduction, possession or use of this product by the general public is restricted by Regulation (EU) 2019/1148. All suspicious transactions, and significant disappearances and thefts should be reported to the relevant national contact point.

VOC content Directive 2010/75/EU

| VOC content | Remark | |
|-------------|----------------------------|--|
| | Not applicable (inorganic) | |

Directive 2012/18/EU (Seveso III)

Not subject to registration according to Directive 2012/18/EU (Seveso III)

European drinking water standards (98/83/EC and 2020/2184)

sulfuric acid, conc=93-99.5%

| Parameter | Parametric value | Note | Reference | | |
|-----------|------------------|------|---|--|--|
| Sulphate | 250 mg/l | | Listed in Annex I, Part C, of Directive (EU) 2020/2184 on the | | |
| | | | quality of water intended for human consumption. | | |

REACH Annex XVII - Restriction

Subject to restrictions of Annex XVII of Regulation (EC) No. 1907/2006: restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles.

| | Designation of the substance, of the group of substances or of the mixture | Conditions of restriction | | |
|---|---|---|--|--|
| • sulfuric acid, conc=93-99.5% | Liquid substances or mixtures fulfilling the criteria for any of the following hazard classes or categories set out in Annex 1 to Regulation (EC) No 1272/2008: (a) hazard classes 2.1 to 2.4, 2.6 and 2.7, 2.8 types A and B, 2.9, 2.10, 2.12, 2.13 categories 1 and 2, 2.14 categories 1 and 2, 2.15 types A to F; (b) hazard classes 3.1 to 3.6, 3.7 adverse effects on sexual function and fertility or on development, 3.8 effects other than narcotic effects, 3.9 and 3.10; (c) hazard class 5.1. | Shall not be used in: ornamental articles intended to produce light or colour effects by means of different phases, for example in ornamental lamps and ashtrays, tricks and jokes, games for one or more participants, or any article intended to be used as such, even with ornamental aspects, Articles not complying with paragraph 1 shall not be placed on the market. Shall not be placed on the market if they contain a colouring agent, unless required for fiscal reasons, or perfume, or both, if they: | | |
| on for revision: 4;8;9;11;12 Publication date: 2001-12-29 | | | | |

Date of revision: 2022-06-08

| | | sulfuric acid, co | |
|--|---|---|---|
| | | | are met: a) lamp oils, labelled with H304, intended for supply to the general public are visibly, leg and indelibly marked as follows: "Keep lamps filled with this liquid out of the reach of children"; and, by 1 December 2010, "Just a sip of lamp oil — or even sucking the wick o lamps — may lead to life- threatening lung damage"; b) grill lighter fluids, labelled with H304, intended for supply to the general public are leg and indelibly marked by 1 December 2010 as follows: "Just a sip of grill lighter may lead life threatening lung damage"; c) lamp oils and grill lighters, labelled with H304, intended for supply to the general public are packaged in black opaque containers not exceeding 1 litre by 1 December 2010. |
| ulfuric ac | cid, conc=93-99.5% | Substances falling within one or more of the following points: (a) substances classified as any of the following in Part 3 of Annex VI to Regulation (EC) No 1272/2008: — carcinogen category 1A, 1B or 2, or germ cell mutagen category 1A, 1B or 2, but excluding any such substances classified due to effects only following exposure by inhalation — reproductive toxicant category 1A, 1B or 2 but excluding any such substances classified due to effects only following exposure by inhalation — reproductive toxicant category 1A, 1B or 2 but excluding any such substances classified due to effects only following exposure by inhalation — serious eye damage category 1, 1A or 1B — skin corrosive category 1, 1A or 1B or 1C or skin irritant category 2 (b) substances listed in Annex II to Regulation (EC) No 1223/2009 of the European Parliament and of the Council (c) substances listed in Annex IV to Regulation (EC) No 1223/2009 for which a condition is specified in at least one of the columns g, h and i of the table in that Annex (d) substances listed in Annex. The ancillary requirements in paragraphs 7 and 8 of column 2 of this entry apply to all mixtures for use for tattooing purposes, whether or not they contain a substance falling within points (a) to (d) of this column of | |
| | | this entry. | |
| | | this entry. | |
| | nal legislation Belgium Additional classification | Acide sulfurique (brume); C; La mentior | a protection des travailleurs contre les risques liés à l'exposition à des agents |
| Natior | Additional classification | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. |
| A <u>Natior</u> | Additional classification nal legislation The Netherla Waterbezwaarlijkheid | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox ands A (3); Algemene Beoordelingsmethodie | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. k (ABM) |
| A <u>Natior</u> S | Additional classification | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox ands A (3); Algemene Beoordelingsmethodie zwavelzuurnevels; Listed in SZW-list of | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. k (ABM) |
| Natior V S k Natior | Additional classification nal legislation The Netherla Waterbezwaarlijkheid SZW - Lijst van kankerverwekkende stoffen nal legislation France No data available | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox ands A (3); Algemene Beoordelingsmethodie zwavelzuurnevels; Listed in SZW-list of | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. k (ABM) |
| Natior Natior Natior | Additional classification nal legislation The Netherla Waterbezwaarlijkheid SZW - Lijst van kankerverwekkende stoffen nal legislation France | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox ands A (3); Algemene Beoordelingsmethodie zwavelzuurnevels; Listed in SZW-list of | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. k (ABM) carcinogenic substances |
| Natior S Natior Natior | Additional classification nal legislation The Netherla Waterbezwaarlijkheid SZW - Lijst van kankerverwekkende stoffen nal legislation France No data available nal legislation Germany | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox ands A (3); Algemene Beoordelingsmethodie zwavelzuurnevels; Listed in SZW-list of 8 B: Nicht brennbare ätzende Gefahrsto | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. k (ABM) carcinogenic substances |
| Natior S Natior Natior Natior | Additional classification nal legislation The Netherla Waterbezwaarlijkheid SZW - Lijst van kankerverwekkende stoffen nal legislation France No data available nal legislation Germany Lagerklasse (TRGS510) | Acide sulfurique (brume); C; La mentior royal du 2 décembre 1993 concernant l cancérigènes et mutagènes et reprotox ands A (3); Algemene Beoordelingsmethodie zwavelzuurnevels; Listed in SZW-list of 8 B: Nicht brennbare ätzende Gefahrsto 1; Verordnung über Anlagen zum Umga Schwefeldioxid; Y; Risiko der Fruchtschä Grenzwertes nicht befürchtet zu werde | a protection des travailleurs contre les risques liés à l'exposition à des agents iques au travail. k (ABM) carcinogenic substances offe ing mit wassergefährdenden Stoffen (AwSV) - 18. April 2017 adigung braucht bei Einhaltung des Arbeitsplatzgrenzwertes und des biologisch n |
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Date of revision: 2022-06-08

SECTION 16: Other information

Full text of any H- and EUH-statements referred to under section 3: H314 Causes severe skin burns and eye damage.

H318 Causes serious eye damage.

| (*) | INTERNAL CLASSIFICATION BY BIG |
|--------------|--|
| ADI | Acceptable daily intake |
| AOEL | Acceptable operator exposure level |
| ATE | Acute Toxicity Estimate |
| CLP (EU-GHS) | Classification, labelling and packaging (Globally Harmonised System in Europe) |
| DMEL | Derived Minimal Effect Level |
| DNEL | Derived No Effect Level |
| EC50 | Effect Concentration 50 % |
| ErC50 | EC50 in terms of reduction of growth rate |
| LC50 | Lethal Concentration 50 % |
| LD50 | Lethal Dose 50 % |
| NOAEL | No Observed Adverse Effect Level |
| NOEC | No Observed Effect Concentration |
| OECD | Organisation for Economic Co-operation and Development |
| PBT | Persistent, Bioaccumulative & Toxic |
| PNEC | Predicted No Effect Concentration |
| STP | Sludge Treatment Process |
| vPvB | very Persistent & very Bioaccumulative |

The information in this safety data sheet is based on data and samples provided to BIG. The sheet was written to the best of our ability and according to the state of knowledge at that time. The safety data sheet only constitutes a guideline for the safe handling, use, consumption, storage, transport and disposal of the substances/preparations/mixtures mentioned under point 1. New safety data sheets are written from time to time. Only the most recent versions may be used. Unless indicated otherwise word for word on the safety data sheet, the information does not apply to substances/preparations/mixtures in purer form, mixed with other substances or in processes. The safety data sheet offers no quality specification for the substances/preparations/mixtures in question. Compliance with the instructions in this safety data sheet does not release the user from the obligation to take all measures dictated by common sense, regulations and recommendations or which are necessary and/or useful based on the real applicable circumstances. BIG does not guarantee the accuracy or exhaustiveness of the information provided and cannot be held liable for any changes by third parties. This safety data sheet is only to be used within the European Union, Switzerland, Iceland, Norway and Liechtenstein. Any use outside of this area is at your own risk. Use of this safety data sheet is subject to the licence and liability limiting conditions as stated in your BIG licence agreement or when this is failing the general conditions of BIG. All intellectual property rights to this sheet are the property of BIG and its distribution and reproduction are limited. Consult the mentioned agreement/conditions for details.

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Downstream user exposure scenario for sulphuric acid.

| 1 | Exposure Scenario 1: Production of Sulphuric acid | | | | |
|--|--|--|--|--|--|
| Product | Production of sulphuric acid | | | | |
| Processe | s Covered: | | | | |
| Environ | mental Releases | | | | |
| ERC01: | Manufacture of Substances | | | | |
| Worker | Processes | | | | |
| PROCO2 PROCO3 PROCO4 PROCO8 at non-do PROCO8 at dedica | PROC01: Use in closed process, no likelihood of exposure PROC02: Use in closed process, with some potential for exposure PROC03: Use in closed batch process (synthesis or formulation) PROC04: Use in batch and other process (synthesis) where opportunity for exposure exists. PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities. PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities. PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities. PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities. | | | | |
| Process | Process Category: | | | | |
| PC 19: I | PC 19: Intermediate | | | | |
| from sul fossil fu systems. process i 140°C). | c acid is most commonly manufactured from sulphur (obtained from refining of crude oil) or phur-containing gas released from high temperature processes such as metal smelting or burning els. Sulphuric acid may also be manufactured as a result of sulphur-capture pollution control Several processes may be used to produce sulphuric acid however, the most typical industrial s the contact process. Sulphur dioxide (SO ₂) is produced by combustion of liquid sulphur (S ₂ at The produced sulphuric acid may then be diluted with water or steam condensate to give a f commercial concentrations | | | | |
| | he hazardous and corrosive nature of sulphuric acid the production systems are highly controlled loy closed systems during the production processes. | | | | |

Contributing Environmental Scenario (CES 1): Environmental exposure arising due to production of sulphuric acid (ERC 1).

Contributing Worker Scenarios: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (such as sampling, cleaning, maintenance) (PROC 3)

and PROC 4), CES 5: transfer of substances to and from vessels and containers at non-dedicated facilities (PROC 8a), CES 6: transfer of substances to and from vessels and containers at dedicated facilities (PROC 8b) and CES 7: worker exposure arising due to transfer of formulation to small containers (PROC 9).

1.1

Controlling environmental exposure for ES 1

ES1: Contributing exposure scenario (CES) 1 Environmental exposure arising due to production of sulphuric acid

Section 2.1 describes the environmental releases that may occur during the production of sulphuric acid. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water and sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Production of sulphuric acid is generally continuous with constant production and use. Facilities may generally produce between 100 and 1,500 tonnes per day with up to 1.2million tonnes produced per year at the largest European manufacturing plant. This value has been considered as a worst case assumption for this environmental exposure scenario.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities may generally produce between 100 and 1,500 tonnes per day in a large facility with a working year of 360 days. Up to 1.2million tonnes may be produced per year at the largest European manufacturing plant which is considered to be a worst case assumption.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 33.3 kg/d but are generally much less.

Other operational conditions affecting environmental exposure

Production takes place in a highly specialized indoor facility with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems. Waste gas emissions are scrubbed and may also be diverted to the wastewater stream.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities. Transfer operations are carried out under controlled conditions in sealed systems to reduce potential losses.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid is produced on a large scale, generally on major chemical sites, which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner. Measured pH values can be used to confirm the efficacy of the neutralization procedure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Emissions to the municipal STP should not be made. All waste water should be treated in the on-site waste water treatment plant. Precipitated sludge should be sent for specialized waste treatment and should not be spread to soil.

Conditions and measures related to external treatment of waste for disposal

Sludge from the on-site WWTP would normally be sent to specialized landfill or for incineration at a dedicated waste facility. Waste from any scrubbers should be directed to waste water. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

1.2

Controlling worker exposure for ES 1

ES1: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (such as sampling, cleaning, maintenance) (PROC 3 and PROC 4), CES 5: transfer of substances to and from vessels and containers at non-dedicated facilities (PROC 8a), CES 6: transfer of substances to and from vessels and containers at dedicated facilities (PROC 8b) and CES 7: worker exposure arising due to transfer of formulation to small containers (PROC 9).

During the production of sulphuric acid controlled systems are in place to reduce the potential for worker exposure in all cases.

Road/rail tanker connecting and disconnecting (loading and unloading) generally takes place in the open air. Loading and unloading of tankers with sulphuric acid is performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). Respiratory equipment (P3 filters) should also be worn when required. A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities may generally produce between 100 and 1,500 tonnes per day with up to 1.2million tonnes produced per year at the largest European manufacturing plant considered to be a worst case assumption.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks such as sampling and maintenance are expected to be short duration events. Human factors not influenced by risk management

Respiration volume under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with local exhaust ventilation and vapour recovery systems are in place where required. Transfer operations are carried out in controlled systems with dedicated machinery.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

LEV is in place in the production area during transfer and drum filling. Systems are sealed to prevent losses occurring.

Organizational measures to prevent/limit release

Workers are fully trained in order to prevent accidental release and frequent competency assessments are carried out by supervisors.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure. Respiratory equipment (P3 filter standard) may also be used when required. Air quality is protected by LEV. No consumption of food or liquids is allowed in the production facility.

- 1.3
- **Exposure estimation and reference to its source**

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|--|------------------------|-----------------------------------|
| Freshwater (in mg/L) | 7 x 10 ⁻⁷ | |
| | | |
| Marine water (in mg/L) | 1 x 10 ⁻⁷ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 6.7 x 10 ⁻⁷ | |
| Marine sediment (in mg/kg) | 8.2 x 10 ⁻⁸ | |

| Agricultural soil (averaged over 30 days | 4.7 x 10 ⁻⁵ | |
|---|------------------------|--|
| (in mg/kg) | | |
| Groundwater (in mg/L) | 3.5 x 10 ⁻⁴ | |
| Annual average PEC in air, total (mg/m^3) | 0.0091 | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|------------------------------|------------------------|--------------|------------------------|--------------------------|
| Tier 2 Freshwater | 7 x 10 ⁻⁷ | 0.0025 | 2.8 x 10 ⁻⁴ | Safe use demonstrated |
| Tier 2 Sediment | 6.7 x 10 ⁻⁷ | 0.002 (EPM) | 3.3 x 10 ⁻⁴ | Safe use demonstrated |
| Tier 2 Intermittent releases | | NA | | |
| Tier 2 Marine | 1 x 10 ⁻⁷ | 0.002 (EPM) | 4 x 10 ⁻⁴ | Safe use demonstrated |
| Tier 2 Marine sediment | 8.2 x 10 ⁻⁸ | 0.00025 | 4.1 x 10 ⁻⁵ | Safe use demonstrated |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid associated with ES 1, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 1. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 1 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3, 4, 5, 6 and 7:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|---------------------|-------------------------|--|
| Exposure duration | re duration All 480 min | |
| Product type | All | Liquid (medium viscosity – like oil) |
| Process temperature | PROC 1,2,3,4 | Hot processes (50-150°C) |
| | PROC 8a,8b, 9 | Room temperature (15-25°C) |
| Vapour pressure | All | 6 Pa – Substance is considered to be low volatile, |

| | | exposure to mists is estimated | |
|-----------------------------------|------------------|--|--|
| Liquid weight fraction | All | 0.98 | |
| Primary emission source proximity | PROC 1, 2 | Primary emission source is not located in the breathing | |
| | | zone of the worker - the assessment for this activity | |
| | | involves a primary far-field emission source only | |
| | | (workers are in a control room) | |
| | PROC 3,4,8a,8b,9 | Primary emission source located in the breathing zone of | |
| | | the workers (i.e. Within 1 metre) | |
| Activity class | All | Transfer of liquid products | |
| Containment | PROC 1,2,3,9 | Handling reduces contact between product and adjacent | |
| | | air | |
| | PROC 4 | Open process, submerged loading | |
| | PROC 8a,8b | n/a | |
| Localised controls | PROC 1,3,8b | Vapour recovery systems; LEV | |
| | PROC 2,4,9 | Vapour recovery | |
| | PROC 8a | None | |
| Segregation | PROC 1,2 | Complete segregation of workers in separate control | |
| | | room | |
| Fugative emission source | PROC 1,3,8b,9 | Process fully enclosed – not breached for sampling | |
| | PROC 2,4,8a | Not fully enclosed – effective housekeeping practices in | |
| | | place. | |
| Dispersion | PROC 1,2,8a,8b | Outdoors not close to buildings | |
| | PROC 3,4 | Outdoors close to buildings | |
| | PROC 9 | Indoors, any sized room, only good natural ventilation | |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Production (High integrity closed system, sampling via closed loop) | 1 | Liquid | 8.2 x 10 ⁻¹⁰ | 9.3 x 10 ⁻⁹ | 3.6 x 10 ⁻⁹ | 9.4 x 10 ⁻⁹ |
| Production and sampling (Occasional exposure system) | 2 | Liquid | 8.2 x 10 ⁻⁹ | 9.2 x 10 ⁻⁸ | 3.6 x 10 ⁻⁸ | 9.2 x 10 ⁻⁸ |
| Production, transfer and sampling | 3 | Liquid | 3.7 x 10 ⁻⁵ | 4.2 x 10 ⁻⁴ | 1.6 x 10 ⁻⁴ | 4.2 x 10 ⁻⁴ |
| Production, transfer and sampling (Exposure likely) | 4 | Liquid | 1.2×10^{-3} | 1.4 x 10 ⁻² | 5.4 x 10 ⁻³ | 1.4 x 10 ⁻² |
| Loading/transfer | 8a | Liquid | 2.0 x 10 ⁻³ | 2.3 x 10 ⁻² | 8.8 x 10 ⁻² | 2.3 x 10 ⁻² |
| Loading/transfer | 8b | Liquid | 1.1 x 10 ⁻⁵ | 1.2 x 10 ⁻⁴ | 4.8 x 10 ⁻⁵ | 4.8 x 10 ⁻⁶ |
| Loading/transfer (Small containers) | 9 | Liquid | 8.1 x 10 ⁻⁴ | 3.2×10^{-3} | 3.2 x 10 ⁻³ | 2.8 x 10 ⁻³ |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 1- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |
| | CES 3 | PROC 2 | 9.2 x 10-8 | Respiratory irritation and corrositivity | 0.1 | 4.2 x 10 ⁻³ |
| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻¹ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.2 x 10 ⁻³ |
| | CES 6 | PROC 8b | 1.2 x10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 3.2 x-10 ⁻² |
| | CES 7 | PROC 9 | 3.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 9.2 x-10 ⁻⁷ |
| Long-term – local effects | CES 2 | PROC 1 | 9.4 x10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 1.8 x10 ⁻⁶ |
| | CES 3 | PROC 2 | 9.2 x10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 4.6 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |
| | CES 6 | PROC 8b | 4.8 x 10 ⁻⁶ | Respiratory irritation and corrositivity | 0.05 | 5.6 x10 ⁻² |
| | CES 7 | PROC 9 | 2.8×10^{-3} | Respiratory irritation and corrositivity | 0.05 | 1.8 x10 ⁻⁶ |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and

so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The first aspect of the OCs that reduces the risk of dermal contact is the specialised nature of the systems involved and the degree of closure associated with them. All pipes and transfers lines are closed and sealed in order to reduce any possible exposure to leaks or splashes. The reactors themselves are similarly closed and sealed in order to reduce any possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are utilised in order to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be employed in certain circumstances where large volumes and high concentrations are required. Training and certification plays an important part in ensuring the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emission are not circumvented and so proper function can be maintained.

In addition to the measures in place to reduce system emission worker segregation also plays an important part in the reduction of risk in the industrial setting. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures would range from procedural policies which are in place to guide workers with respect to proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

In order to further protect the worker personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers in large scale industrial production and use plants is adequately managed.

| | ed above when the concentration of the acid decreases so does the potential for chemical nan skin. However the same measures are still in place to ensure that professionals and |
|---|--|
| | protected from risk. |
| 1.4 | Guidance to DU to evaluate whether he works inside the boundaries set by the ES |
| Environme | ntal releases: |
| In order to v | vork within the boundaries of the ES the following conditions should be met: |
| No eThe | ession to air after scrubbing less than 33.3 kg per day emission to the municipal STP industrial WWTP sludge should not be spread to soil |
| | tewater should be fully neutralized sured emissions should be confirmed to be less than the relevant PNECs in section 3 |
| Worker exj | posure: |
| In order to v | vork within the boundaries of the ES the following conditions should be met: |
| LEVWor prod | etors and pipelines should be sealed systems I should be in place in the production facility and in transfer areas kers should wear RPE, protective gloves, goggles, overalls and boots at all times in the uction and transfer area measured exposure should be confirmed to be less than the relevant DNELs in section 3 re |
| 1.5 | Additional good practice advice beyond the REACH CSA. |
| Alw surfa Wor Proc Mac Efficiency | not eat, drink or smoke when working with sulphuric acid. ays wash hands and exposed skin thoroughly after using sulphuric acid or any aces/machinery that may have come into contact with sulphuric acid. kers should be suitably trained in all safety procedures edural and safety compliance should be routinely assessed by management hinery should be regularly maintained and checked for proper function cacy of all emission RMMs and waste treatment procedures should be routinely assessed and irmed to be functioning correctly |
| | xposure Scenario 2: Use of Sulphuric Acid as an Intermediate in manufacture of organic and organic chemicals, including fertilizers. |
| | huric Acid as an Intermediate in manufacture of inorganic and organic chemicals, |

Processes Covered:

Environmental Releases

ERC6A: Industrial use resulting in manufacture of another substance (use of intermediates)

Worker Processes

PROC01: Use in closed process, no likelihood of exposure

PROC02: Use in closed process, with some potential for exposure

PROC03: Use in closed batch process (synthesis or formulation)

PROC04: Use in batch and other process (synthesis) where opportunity for exposure arises.

PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC09: Transfer of formulations or preparations to small containers

Produce Category

PC19: Intermediate

The use of sulphuric acid as an intermediate in the production of inorganic and organic chemicals including but not limited to the production of fertilizers includes the production of oils used for lipolysis, sulphates, nitrogen fertilizers, granulation of complex fertilizers, phosphoric acid (wet process), titanium dioxide (sulphate route), hydrofluoric acid, fine chemicals and speciality chemicals. Sulphuric acid is also used as an intermediate for reactive use in water treatment, use as a granulating agent and use as a tanning agent whereas sulphuric acid is consumed in a chemical synthesis to form sulphate.

Due to the hazardous and corrosive nature of sulphuric acid when used as an intermediate, the process is conducted under highly controlled conditions.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of Sulphuric Acid as an Intermediate in manufacture of inorganic and organic chemicals, including fertilizers (ERC 6A).

Contributing Worker Scenarios: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4), CES 5: worker exposure arising due transfer of substances to large vessels at non-dedicated and dedicated facilities (PROC 8a and PROC 8b) and CES 6: worker exposure arising due to transfer of formulation to small containers (PROC 9).

2.1

Controlling environmental exposure for ES 2

ES1: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of Sulphuric Acid as an Intermediate in manufacture of inorganic and organic chemicals, including fertilizers.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid as an intermediate. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid as an intermediate is generally continuous with constant production and use. Facilities generally use between 100 and 500 tonnes per day in a large facility, with 300,000 tonnes per year used as a worst case assumption.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 100 and 500 tonnes per day in a large facility with a working year of 360 days. Up to 1.2million tonnes may be produced per year at the largest European manufacturing plant which is considered to be a worst case assumption.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 94.9 kg/d but are generally much less. Exhaust gases may be treated by scrubbers.

Other operational conditions affecting environmental exposure

Intermediate use of sulphuric acid takes place in a highly specialized indoor facility with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities. Transfer operations are carried out under controlled conditions in sealed systems to reduce potential losses.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used as an intermediate on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner. Measured pH values can be used to confirm the efficacy of the neutralization procedure.

Organizational measures to prevent/limit releases from site

Annex - page 11

Workers are fully trained in order to prevent accidental release. pH alarms are in place to monitor the

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pH and ensure successful neutralization has taken place.

Conditions and measures related to municipal STP

Emissions to the municipal STP should not be made. All waste water should be treated in the on-site waste water treatment plant. Precipitated sludge should be sent for specialized waste treatment and should not be spread to soil.

Conditions and measures related to external treatment of waste for disposal

Sludge from the on-site WWTP would normally be sent to specialized landfill or for incineration at a dedicated waste facility. Waste from any scrubbers should be directed to waste water. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

2.2

Controlling worker exposure for ES 2

ES2: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4), CES 5: worker exposure arising due transfer of substances to large vessels at non-dedicated and dedicated facilities (PROC 8a and PROC 8b) and CES 6: worker exposure arising due to transfer of formulation to small containers (PROC 9).

During the use of sulphuric acid as an intermediate, controlled systems are in place to reduce the potential for worker exposure in all cases.

Road/rail tanker connecting and disconnecting (loading and unloading) generally takes place in the open air. Loading and unloading of tankers with sulphuric acid is performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). Respiratory protection is used when required. A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 100 and 500 tonnes per day in a large facility with a working year of 360 days. Up to 1.2million tonnes may be produced per year at the largest European manufacturing plant which is considered to be a worst case assumption.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance will only be of a short duration. Human factors not influenced by risk management

Respiration volumes under conditions of use 10m³/d (default value for

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for a 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with local exhaust ventilation and vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and

controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered) in the areas where sulphuric acid is used as an intermediate. During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in the sampling and transfer of materials to road tankers are fully trained in order to prevent accidental release and frequent competency assessments are carried out by supervisors. Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure. Appropriate respiratory equipment is also worn when required.

| - | - |
|---|---|
| 1 | |
| | • |

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|--|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 8.8 x 10 ⁻⁴ | |
| Marine water (in mg/L) | 1.2 x 10 ⁻⁴ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 7.13 x 10 ⁻⁴ | |
| Marine sediment (in mg/kg) | 1.03 x 10 ⁻⁴ | |
| Agricultural soil (averaged over 30 days (in mg/kg) | 0.0149 | |
| Groundwater (in mg/L) | 0.11 | |
| Annual average PEC in air, total (mg/m ³) | 0.0261 | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|-------------------|------------------------|--------------|----------|-----------------------|
| Tier 2 Freshwater | 8.8 x 10 ⁻⁴ | 0.0025 | 0.352 | Safe use demonstrated |
| Tier 2 Sediment | 7.3 x 10 ⁻⁴ | 0.002 (EPM) | 0.365 | Safe use |

| | | | | demonstrated |
|------------------------------|-------------------------|-------------|-------|-----------------------|
| Tier 2 Intermittent releases | | NA | | |
| Tier 2 Marine | 1.2 x 10 ⁻⁴ | 0.00025 | 0.48 | Safe use demonstrated |
| Tier 2 Marine sediment | 1.03 x 10 ⁻⁴ | 0.002 (EPM) | 0.051 | Safe use demonstrated |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 2, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 2. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 2 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3, 4, 5 and 6:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|------------------|---|
| Exposure duration | All | 480 min |
| Product type | All | Liquid (medium viscosity – like oil) |
| Process temperature | PROC 1,2,3,4 | Hot processes (50-150°C) |
| | PROC 8a,8b, 9 | Room temperature (15-25°C) |
| Vapour pressure | All | 6 Pa – Substance is considered to be low volatile, exposure |
| | | to mists is estimated |
| Liquid weight fraction | All | 0.98 |
| Primary emission source proximity | PROC 1,2 | Primary emission source is not located in the breathing |
| | | zone of the worker - the assessment for this activity |
| | | involves a primary far-field emission source only (workers |
| | | are in a control room) |
| | PROC 3,4,8a,8b,9 | Primary emission source located in the breathing zone of |
| | | the workers (i.e. Within 1 metre) |
| Activity class | All | Transfer of liquid products |
| Containment | PROC 1,2, 3,9 | Handling reduces contact between product and adjacent |
| | | air. |
| | PROC 4 | Open process, submerged loading |
| | PROC 8a,8b | n/a |

| Localised controls | PROC1,3,8b | Vapour recovery systems; LEV |
|--------------------------|----------------|--|
| | PROC 2,4,9 | Vapour recovery |
| | PROC 8a | None |
| Segregation | PROC 1,2 | Complete segregation of workers in separate control room |
| Fugative emission source | PROC 1,3,8b,9 | Process fully enclosed – not breached for sampling |
| | PROC 2,4,8a | Not fully enclosed – effective housekeeping practices in |
| | | place. |
| Dispersion | PROC 1,2,8a,8b | Outdoors not close to buildings |
| | PROC 3,4 | Outdoors near to buildings |
| | PROC 9 | Indoors, any sized room, only good natural ventilation |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed process, no likelihood of exposure | 1 | Liquid | 8.2 x 10 ⁻¹⁰ | 9.3 x 10 ⁻⁹ | 3.6 x 10 ⁻⁹ | 9.4 x 10 ⁻⁹ |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 8.2 x 10 ⁻⁹ | 9.2 x 10 ⁻⁸ | 3.6 x 10 ⁻⁸ | 9.2 x 10 ⁻⁸ |
| Use in closed batch process (synthesis or formulation) | 3 | Liquid | 3.7 x 10 ⁻⁵ | 4.2×10^{-4} | 1.6 x 10 ⁻⁴ | 4.2 x 10 ⁻⁴ |
| Use in batch and other process (synthesis) where opportunity for exposure arises | 4 | Liquid | 1.2 x 10 ⁻³ | 1.4 x 10 ⁻² | 5.4 x 10 ⁻³ | 1.4 x 10 ⁻² |
| Loading/transfer | 8a | Liquid | 2.0 x 10 ⁻³ | 2.3 x 10 ⁻² | 8.8 x 10 ⁻² | 2.3 x 10 ⁻² |
| Loading/transfer | 8b | Liquid | 1.1 x 10 ⁻⁵ | 1.2 x 10 ⁻⁴ | 4.8 x 10 ⁻⁵ | 4.8 x 10 ⁻⁶ |
| Loading/transfer (Small containers) | 9 | Liquid | 8.1 x 10 ⁻⁴ | 3.2×10^{-3} | 3.2 x 10 ⁻³ | 2.8 x 10 ⁻³ |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 2- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|---------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.1 | 4.2 x 10 ⁻³ |
| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻¹ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻¹ |

| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.2×10^{-3} |
|------------------------------|-------|---------|------------------------|--|------|------------------------|
| | | PROC 8b | 1.2 x10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 3.2 x-10 ⁻² |
| | CES 6 | PROC 9 | 3.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 9.2 x- 10^{-7} |
| Long-term – local effects | CES 2 | PROC 1 | 9.4 x10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 1.8 x10 ⁻⁶ |
| | CES 3 | PROC 2 | 9.2 x10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 4.6 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |
| | | PROC 8b | 4.8 x 10 ⁻⁶ | Respiratory irritation and corrositivity | 0.05 | 5.6 x10 ⁻² |
| | CES6 | PROC 9 | 2.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 1.8 x10 ⁻⁶ |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas

displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

2.4

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 94.9 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Exhaust gases from the intermediate use are treated with scrubbers.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- LEV should be in place in the production facility and in transfer areas
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area
- Appropriate respiratory equipment should also be worn if required.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above
- Submerged loading can be used to reduce the amount of aerosol formation.

| 2.5 | Additional good practice advice beyond the REACH CSA. |
|---|---|
| Alw surfa Wor All l integ Proc Mac Efficient | not eat, drink or smoke when working with sulphuric acid. ays wash hands and exposed skin thoroughly after using sulphuric acid or any aces/machinery that may have come into contact with sulphuric acid. kers should be suitably trained in all safety procedures PPE should be properly maintained and stored in an appropriate way so as not to damage its grity. Workers should be correctly trained in its use. redural and safety compliance should be routinely assessed by management whinery should be regularly maintained and checked for proper function cacy of all emission RMMs and waste treatment procedures should be routinely assessed and firmed to be functioning correctly |

3 Exposure Scenario 3: Use of Sulphuric Acid as a Processing aid, catalyst, dehydrating agent and pH regulator.

Use of Sulphuric Acid as a Processing aid, catalyst, dehydrating agent and pH regulator.

Processes Covered:

Environmental Releases

ERC6B: Industrial use of reactive processing aids.

Worker Processes

PROC01: Use in closed process, no likelihood of exposure PROC02: Use in closed process, with some potential for exposure

PROC03: Use in closed batch process (synthesis or formulation)

PROC04: Use in batch and other process (synthesis) where opportunity for exposure arises.

PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC09: Transfer of formulations or preparations to small containers

PROC13: Treatment of articles by dipping and pouring.

Produce Category

PC20: Products such as pH-regulators, flocculants, precipitants, neutralization agents.

Sulphuric acid is used in the industrial manufacture of organic chemicals and fine chemicals. These processes include using sulphuric acid in large volumes as a processing aid, catalyst or dehydration agent in the chemical process of manufacture of adhesives, explosives, acids, organic salts, dyes and pigments, biofuels, pharmaceuticals and the alkylation of aliphatics. Sulphuric acid may also be used to regulate pH in water streams and as a process aid in the leather and textiles industry.

Due to the hazardous and corrosive nature of sulphuric acid when used as a processing aid, the process is conducted under highly controlled conditions.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of Sulphuric Acid as a Processing aid, catalyst, dehydrating agent and pH regulator. (ERC 6B).

Contributing Worker Scenarios: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4), CES 5: worker exposure arising due transfer of substances to large vessels at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 6: worker exposure arising due to transfer of formulation to small containers (PROC 9) and CES 7: worker exposure arising due to treatment of articles by dipping and pouring.

3.1 Controlling environmental exposure for ES 3

ES3: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of Sulphuric Acid as a processing aid, catalyst, dehydrating agent and pH regulator.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid as a processing aid, catalyst, dehydrating agent or pH regulator. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in

the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid as a processing aid, catalyst, dehydrating agent or pH regulator is generally continuous with constant production and use. Facilities generally use between 100 and 500 tonnes per day in a large facility, with 100,000 tonnes per year used as a worst case assumption.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 100 and 500 tonnes per day in a large facility with a working year of 360 days. Up to 100,000 tonnes may be produced per year at the largest European manufacturing plant which is considered to be a worst case assumption.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 333 kg/d but are generally much less. Exhaust gases may be treated by scrubbers.

Other operational conditions affecting environmental exposure

The use of sulphuric acid as a processing aid, catalyst, dehydrating agent or pH regulator takes place in a highly specialized, high integrity indoor facility with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities. Transfer operations are carried out under controlled conditions in sealed systems to reduce potential losses.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used as a processing aid, catalyst, dehydrating agent or pH regulator on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner. Measured pH values can be used to confirm the efficacy of the neutralization procedure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release. pH alarms are in place to monitor the pH and ensure successful neutralization has taken place.

Conditions and measures related to municipal STP

Emissions to the municipal STP should not be made. All waste water should be treated in the on-site waste water treatment plant. Precipitated sludge should be sent for specialized waste treatment and should not be spread to soil.

Conditions and measures related to external treatment of waste for disposal

Sludge from the on-site WWTP would normally be sent to specialized landfill or for incineration at a dedicated waste facility. Waste from any scrubbers should be directed to waste water. There is no

further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

3.2

Controlling worker exposure for ES 3

ES3: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4), CES 5: worker exposure arising due transfer of substances to large vessels at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 6: worker exposure arising due to transfer of formulation to small containers (PROC 9) and CES 7: worker exposure arising due to treatment of articles by dipping and pouring.

During the use of sulphuric acid as a processing aid, catalyst, dehydrating agent or pH regulator, controlled systems are in place to reduce the potential for worker exposure in all cases.

Road/rail tanker connecting and disconnecting (loading and unloading) generally takes place in the open air. Loading and unloading of tankers with sulphuric acid is performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). Respiratory protection is used when required. A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover. Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 100 and 500 tonnes per day in a large facility with a working year of 360 days. Up to 100,000 tonnes may be produced per year at the largest European manufacturing plant which is considered to be a worst case assumption.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance will only be of a short duration.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for a 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with local exhaust ventilation and vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered) in the areas where sulphuric acid is used as a processing aid, catalyst, dehydrating agent or pH regulator. During handling when transferring drum filling, special equipment and controlled systems

with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in the sampling and transfer of materials to road tankers are fully trained in order to prevent accidental release and frequent competency assessments are carried out by supervisors.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

- 3.3
- **Exposure estimation and reference to its source**

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|--|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 5.91 x 10 ⁻⁶ | |
| Marine water (in mg/L) | 8.56 x 10 ⁻⁷ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 4.8 x 10 ⁻⁶ | |
| Marine sediment (in mg/kg) | 6.9 x 10 ⁻⁷ | |
| Agricultural soil (averaged over 30 days (in mg/kg) | 3.9 x 10 ⁻⁴ | |
| Groundwater (in mg/L) | 2.9 x 10 ⁻³ | |
| Annual average PEC in air, total (mg/m ³) | 0.0091 | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|------------------------------|-------------------------|--------------|-------------------------|--------------------------|
| Tier 2 Freshwater | 5.9 x 10 ⁻⁶ | 0.0025 | 2.3 x 10 ⁻³ | Safe use demonstrated |
| Tier 2 Sediment | 4.75 x 10 ⁻⁶ | 0.002 (EPM) | 2.35 x 10 ⁻³ | Safe use demonstrated |
| Tier 2 Intermittent releases | | NA | | |
| Tier 2 Marine | 8.56 x 10 ⁻⁷ | 0.00025 | 3.4 x 10 ⁻³ | Safe use demonstrated |

| 4×10 | | 0.002 (EPM) | 6.9 x 10 ⁻⁷ | Tier 2 Marine sediment | er 2 dim | ediment 6.9 x 10 0.002 (EPM) |
|---------------|--|-------------|------------------------|---------------------------|-------------|------------------------------|
|---------------|--|-------------|------------------------|---------------------------|-------------|------------------------------|

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 3, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 3. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 3 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3, 4, 5, 6 and 7:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|----------------------|---|
| Exposure duration | All | 480 min |
| Product type | All | Liquid (medium viscosity – like oil) |
| Process temperature | PROC 1,2,3,4 | Hot processes (50-150°C) |
| | PROC 8a,8b, 9,13 | Room temperature (15-25°C) |
| Vapour pressure | All | 6 Pa – Substance is considered to be low volatile, |
| | | exposure to mists is estimated |
| Liquid weight fraction | All | 0.98 |
| Primary emission source proximity | PROC 1,2 | Primary emission source is not located in the breathing |
| | | zone of the worker - the assessment for this activity |
| | | involves a primary far-field emission source only |
| | | (workers are in a control room) |
| | PROC 3,4,8a,8b,9,13 | Primary emission source located in the breathing zone |
| | | of the workers (i.e. Within 1 metre) |
| Activity class | PROC 1,2,3,4,8a,8b,9 | Transfer of liquid products |
| | PROC 13 | Activities with open liquid surface or reservoirs |
| Containment | PROC 1,2, 3,9 | Handling reduces contact between product and adjacent |
| | | air |
| | PROC 4 | Open process, submerged loading |
| | PROC 8a,8b,13 | n/a |
| Localised controls | PROC1,2,3,8b | Vapour recovery systems; LEV |
| | PROC 2,4,9 | Vapour recovery |
| | PROC 8a,13 | None |
| Segregation | PROC 1,2 | Complete segregation of workers in separate control |
| | | room |

| Fugative emission source | | PROC 1,3,8b,9 | | Process fully enclosed – not breached for sampling | | | |
|---|----------|---------------------------------------|------------------|--|--------------------------|----------------------------------|----------------------------|
| | | PROC 2,4,8a,1 | | Not fully enclosed – effective housekeeping practices | | | |
| | - | | | in place. | | | |
| Dispersion |] | PROC 1,2,8a,8b | | | loors not close to b | uildings | |
| Ĩ | | PROC 3,4 | | | loors near to building | | |
| | | PROC 9,13 | | | ors, any sized roon | | ural ventilation |
| | | | | | , , | -,, 8 | |
| List of derived exposure | concenti | rations | | | | | |
| List of derived exposure | concent | anons | | | | | |
| Description of activity | PROC | PROC Physical state of material | | Estimated Short-term Exposure Concentrations (mg/m3) | | Estimated Exposure (mg/m3) | Long-term Concentration |
| | | | 50 th | | 90 th | 50 th | 90 th |
| | | | | 41. | | | 10 |
| | | | percent value | tile | percentile value | percentile value | percentile value |
| Use in closed process, no | 1 | Liquid | 8.20 x 1 | 0-10 | 9.30 x 10 ⁻⁰⁹ | 3.60 x 10 ⁻⁰⁹ | 9.40 x 10 ⁻⁰⁹ |
| likelihood of exposure | 1 | Liquid | 0.20 X | 0 | 9.30 x 10 | 5.00 x 10 | 9.40 X 10 |
| Use in closed, continuous | 2 | Liquid | 8.20 x 1 | 0-09 | 9.20 x 10 ⁻⁰⁸ | 3.60 x 10 ⁻⁰⁸ | 9.20 x 10 ⁻⁰⁸ |
| process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 0.20 x 1 | | 7.20 X 10 | 5.00 x 10 | 9.20 X 10 |
| Use in closed batch process (synthesis or formulation) | 3 | Liquid | 3.70 x 1 | 0-05 | 4.20 x 10 ⁻⁰⁴ | 1.60 x 10 ⁻⁰⁴ | 4.20 x 10 ⁻⁰⁴ |
| Use in batch and other process (synthesis) where opportunity for exposure arises | 4 | Liquid | 1.2 x 10 | | 0.014 | 0.0054 | 0.014 |
| Loading/transfer: Loading and unloading a tanker (non- dedicated site) | 8a | Liquid | 2.0 x 10 | | 0.023 | 0.0088 | 0.023 |
| Loading/transfer: Loading and unloading a tanker (dedicated site) | 8b | Liquid | 1.10 10 | | 1.20 x 10 ⁻⁰⁴ | 4.80 x 10 ⁻⁰⁵ | 4.80 x 10 ⁻⁰⁶ |
| Loading/transfer (filling small containers with sulphuric acid) | 9 | Liquid | 8.1 x 10 | | 0.0032 | 0.0011 | 0.0028 |
| Treatment of articles by dipping and pouring (immersion operations) | 13 | Liquids | 4.5x 10 | -3 | 0.018 | 0.0062 | 0.016 |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 3- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.3 x 10 ⁻⁸ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |



| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 4.2×10^{-3} |
|------------------------------|-------|---------|------------------------|--|------|------------------------|
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻¹ |
| | | PROC 8b | 1.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.2 x 10 ⁻³ |
| | CES 6 | PROC 9 | 3.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 3.2 x 10 ⁻² |
| | CES 7 | PROC 13 | 1.8 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.8 x 10 ⁻¹ |
| Long-term – local effects | CES 2 | PROC 1 | 3.6 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 1.9 x 10 ⁻⁷ |
| | CES 3 | PROC 2 | 3.6 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 1.8 x 10 ⁻⁶ |
| | CES 4 | PROC 3 | 1.6 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | | PROC 4 | 5.4 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 8.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 4.6 x 10 ⁻¹ |
| CES | | PROC 8b | 4.8 x 10 ⁻⁵ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |
| | CES6 | PROC 9 | 1.1 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 5.6 x 10 ⁻² |
| | CES 7 | PROC 13 | 6.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 3.2 x 10 ⁻¹ |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

| 3 | 4 | |
|---|---|--|

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 333 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Exhaust gases from the intermediate use are treated with scrubbers.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area
- Appropriate respiratory equipment should also be worn if required.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 3.5 | Additional good practice advice beyond the REACH CSA. |
|--|---|
| Alw surfa Wor All 1 integ Proce | not eat, drink or smoke when working with sulphuric acid. Tays wash hands and exposed skin thoroughly after using sulphuric acid or any aces/machinery that may have come into contact with sulphuric acid. Takers should be suitably trained in all safety procedures PPE should be properly maintained and stored in an appropriate way so as not to damage its grity. Workers should be correctly trained in its use. Takedural and safety compliance should be routinely assessed by management chinery should be regularly maintained and checked for proper function |
| | cacy of all emission RMMs and waste treatment procedures should be routinely assessed and |

• Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

4 Exposure Scenario 4: Use of Sulphuric Acid for extractions and processing of minerals and ores

Use of Sulphuric Acid for extractions and processing of minerals and ores.

Processes Covered:

Environmental Releases

ERC04: Industrial use of processing aids in processes and products, not becoming part of articles ERC06B: Industrial use of reactive processing aids.

Worker Processes

PROC02: Use in closed process, with some potential for exposurePROC03: Use in closed batch process (synthesis or formulation)PROC04: Use in batch and other process (synthesis) where opportunity for exposure arises.

Produce Category

PC20: Products such as pH-regulators, flocculants, precipitants, neutralization agents. PC40: Extraction agents

Sulphuric acid is used in industrial extraction of and processing of minerals and ores. This use includes leaching, dissolution and enrichment of ores including zinc, copper, nickel and uranium. Metal removal from sand and clay and titanium limonite leaching are also encompassed under this use. Sulphuric acid is utilised in this exposure scenario as a method of mineral and ore leaching and extraction. Ores and minerals are usually leached with sulphuric acid using specialised leaching systems which employs sulphuric acid to dissolve the ores or minerals from their substrate. This process may be performed in ore/mineral piles in the open. The sulphuric acid can then be stripped of its ore or minerals and can then be re-circulated and re-used. Though the acid is intended to react with the substrates a portion of the acid involved may remain un-reacted.

Due to the hazardous and corrosive nature of sulphuric acid when used as a processing aid, the process is conducted under highly controlled conditions.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of Sulphuric Acid for extractions and in the processing of minerals and ores. (ERC 4 and ERC 6B).

Contributing Worker Scenarios: CES 2: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2) and CES 3: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4).

4.1

Controlling environmental exposure for ES 4

ES4: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of Sulphuric Acid for extractions and in the processing of minerals and ores.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid for extractions and in the processing of minerals and ores. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by

designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid in the processing of minerals and ores is generally continuous with constant production and use. Facilities may use up to 480 tonnes per year, considered to be a worst case assumption.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities may use up to 480 tonnes per year, considered to be a worst case assumption.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 1.2 kg/d but are generally much less. Exhaust gases may be treated by scrubbers.

Other operational conditions affecting environmental exposure

The use of sulphuric acid for extractions and in the processing of minerals and ores takes place in a highly specialized, high integrity indoor facility with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used for extractions and in the processing of minerals and ores on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner. Measured pH values can be used to confirm the efficacy of the neutralization procedure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release. pH alarms are in place to monitor the pH and ensure successful neutralization has taken place.

Conditions and measures related to municipal STP

Emissions to the municipal STP should not be made. All waste water should be treated in the on-site waste water treatment plant. Precipitated sludge should be sent for specialized waste treatment and should not be spread to soil.

Conditions and measures related to external treatment of waste for disposal

Sludge from the on-site WWTP is collected and processed for residual metal recovery, incinerated or sent for recovery. Waste from any scrubbers should be directed to waste water. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

4.2

Controlling worker exposure for ES 4

ES4: CES 2: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2) and CES 3: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4).

During the use of sulphuric acid in the processing of minerals and ores, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of tankers with sulphuric acid is performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). Respiratory protection is used when required. A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities may use up to 480 tonnes per year, considered to be a worst case assumption.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance are expected to be of a short duration. Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered) in the areas where sulphuric acid is used in the processing of minerals and ores. During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in the sampling and workers involved in extraction work are generally separated from the leaching and extraction heaps and systems with no direct contact to the acid. Workers involved in

sampling and transfer of materials (new or waste acids to be recycled) to road tankers are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

4.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 5.91 x 10 ⁻⁶ | |
| Marine water (in mg/L) | 8.56 x 10 ⁻⁷ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 4.8 x 10 ⁻⁶ | |
| Marine sediment (in mg/kg) | 6.9 x 10 ⁻⁷ | |
| Agricultural soil (averaged over 30 days (in mg/kg) | 3.9 x 10 ⁻⁴ | |
| Groundwater (in mg/L) | 2.9 x 10 ⁻³ | |
| Annual average PEC in air, total (mg/m ³) | 0.0091 | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|----------------------------------|------------------------|--------------|------------------------|---------------------------------------|
| ERC 6B Tier 2 Freshwater | 2.6 x 10 ⁻⁸ | 0.0025 | 1.1 x 10 ⁻⁴ | Safe use demonstrated in tier 2 |
| ERC 6B Tier 2 Sediment | 2 x 10 ⁻⁸ | 0.002 (EPM) | 1 x 10 ⁻⁵ | Safe use demonstrated in tier 2 |
| ERC 6B Tier 2 Marine sediment | 3 x 10 ⁻⁹ | 0.002 (EPM) | 1 x 10 ⁻⁶ | Safe use demonstrated in tier 2 |
| ERC 6B Tier 2 | 3.8 x 10 ⁻⁹ | 0.00025 | 1.5 x 10 ⁻⁵ | Safe use |

| Marine | | | | demonstrated in tier 2 |
|-----------------------------|------------------------|-------------|--------|---------------------------------------|
| ERC 4Tier 2 Freshwater | 2.5 x 10 ⁻⁵ | 0.0025 | 0.01 | Safe use demonstrated in tier 2 |
| ERC 4Tier 2 Sediment | 2 x 10 ⁻⁵ | 0.002 (EPM) | 0.01 | Safe use demonstrated in tier 2 |
| ERC 4Tier 2 Marine sediment | 2.9 x 10 ⁻⁶ | 0.002 (EPM) | 0.0145 | Safe use demonstrated in tier 2 |
| ERC 4Tier 2 Marine | 3.6 x 10 ⁻⁶ | 0.00025 | 0.0144 | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 4, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 4. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 4 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2 and 3:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|--------|--------------------------------------|
| Exposure duration | All | 480 mins |
| Product type | All | Liquid (medium viscosity – like oil) |
| Process temperature | All | Hot processes (50-150oC) |
| Vapour pressure | All | 6 Pa – Substance is considered to be |
| | | low volatile, exposure to mists is |
| | | estimated |
| Liquid weight fraction | All | 0.98 |
| Primary emission source proximity | PROC 2 | Primary emission source is not |
| | | located in the breathing zone of the |
| | | worker - the assessment for this |

| | | activity involves a primary far-field emission source only (workers are in a control room) |
|--------------------------|----------|--|
| | PROC 3,4 | Primary emission source located in the breathing zone of the workers (i.e. Within 1 metre) |
| Activity class | All | Transfer of liquid products |
| Containment | PROC 2,3 | Handling reduces contact between product and adjacent air |
| | PROC 4 | Open process, submerged loading |
| Localised controls | PROC 2 | Vapour recovery systems; LEV |
| | PROC 2,4 | Vapour recovery |
| Segregation | PROC 2 | Complete segregation of workers in separate control room |
| Fugitive emission source | PROC 3 | Process fully enclosed – not breached for sampling |
| | PROC 2,4 | Not fully enclosed – effective housekeeping practices in place. |
| Dispersion | PROC 2 | Outdoors not close to buildings |
| | PROC 3,4 | Outdoors near to buildings |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 8.20 x 10 ⁻⁰⁹ | 9.20 x 10 ⁻⁰⁸ | 3.60 x 10 ⁻⁰⁸ | 9.20 x 10 ⁻⁰⁸ |
| Use in closed batch process (synthesis or formulation) | 3 | Liquid | 3.70 x 10 ⁻⁰⁵ | 4.20×10^{-04} | 1.60 x 10 ⁻⁰⁴ | 4.20 x 10 ⁻⁰⁴ |
| Use in batch and other process (synthesis) where opportunity for exposure arises | 4 | Liquid | 0.0012 | 0.014 | 0.0054 | 0.014 |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 4- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |
| | CES 3 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 4.2 x 10 ⁻³ |

| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻¹ |
|------------------------------|-------|--------|------------------------|--|------|------------------------|
| Long-term – local effects | CES 2 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 1.8 x 10 ⁻⁶ |
| | CES 3 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work

practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

4.4

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 1,140 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Exhaust gases from the intermediate use are treated with scrubbers.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area
- Workers should be segregated from the area of use.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

4.5 Additional good practice advice beyond the REACH CSA.

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

| 5 | Exposure Scenario 5: Use of Sulphuric Acid in surface treatments, purification and |
|---|--|
| | etching. |

Use of Sulphuric Acid in surface treatments, purification and etching.

Processes Covered:

Environmental Releases

ERC06B: Industrial use of reactive processing aids.

Worker Processes

PROC01: Use in closed process, no likelihood of exposure

PROC02: Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance)

PROC03: Use in closed batch process (synthesis or formulation)

PROC04: Use in batch and other process (synthesis) where opportunity for exposure arises

PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC09: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

PROC13: Treatment of articles by dipping and pouring

Produce Category

PC14: Metal surface treatment products, including galvanic and electroplating products PC15: Non-metal-surface treatment products

Sulphuric acid is used in surface treatment, purification and etching to pickle metallic surface prior to electrolysis in order to remove impurities, stains, rust or other inorganic contaminants. Used pickling fluid is generally neutralised and does not have any consumer application. The processes which use sulphuric acid as metallurgical surface treatments are highly specialised and are controlled to limit emissions and environmental exposure.

Because of the conditions involved in the metal treatment processes (and the nature of sulphuric acid and the produced gases) specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in surface treatment, purification and etching. (ERC 6B).

Contributing Worker Scenarios: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4), CES 5: worker exposure arising due transfer of substances to large vessels at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 6: worker exposure arising due to transfer of formulation to small containers (PROC 9) and CES 7: worker exposure arising due to treatment of articles by dipping and pouring.

5.1 Controlling environmental exposure for ES 5

ES5: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in surface treatment, purification and etching.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in surface treatment, purification and etching. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid in surface treatment, purification and etching is generally continuous with constant production and use. Facilities generally use between 50 and 200 tonnes per year, with utilization of 10,000 tonnes per year at one site considered to be a worst case assumption.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 50 and 200 tonnes per year in a working year of 365 days, with utilization of 10,000 tonnes per year at one site considered to be a worst case assumption. Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 27.4 kg/d but are generally much less. Exhaust gases may be treated by scrubbers.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in surface treatment, purification and etching takes place in a highly specialized, high integrity, contained indoor facility with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used in surface treatment, purification and etching on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner. Measured pH values can be used to confirm the efficacy of the neutralization procedure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste waters are generally treated on site by chemical and/or biological methods before release to the municipal STP or to the environment.

Conditions and measures related to external treatment of waste for disposal

All sludge from onsite WWTP is collected and incinerated or sent to landfill. Waste from any scrubbers should be directed to waste water stream for further treatment. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

5.2

Controlling worker exposure for ES 5

ES5: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due to day to day use in batch or other processes with some potential for exposure (PROC 3 and PROC 4), CES 5: worker exposure arising due transfer of substances to large vessels at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 6: worker exposure arising due to transfer of formulation to small containers (PROC 9) and CES 7: worker exposure arising due to treatment of articles by dipping and pouring.

During the use of sulphuric acid in surface treatment, purification and etching, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of tankers with sulphuric acid for use as a surface treatment and etching agent is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 50 and 200 tonnes per year in a working year of 365 days, with utilization of 10,000 tonnes per year at one site considered to be a worst case assumption.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance and dipping and pouring are expected to be of a short duration.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered) in the areas where sulphuric acid is used in surface treatment, purification and etching. During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in sampling and transfer of materials to road tankers are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

5.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control

environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 5.91 x 10 ⁻⁷ | |
| Marine water (in mg/L) | 8.56 x 10 ⁻⁸ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 2×10^{-8} | |
| Marine sediment (in mg/kg) | 3 x 10 ⁻⁹ | |
| Agricultural soil (averaged over 30 days | 3.94 x 10 ⁻⁵ | |
| (in mg/kg) | | |
| Groundwater (in mg/L) | 2.91 x 10 ⁻⁴ | |
| Annual average PEC in air, total (mg/m ³) | 7.62 x 10 ⁻³ | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|---------------------------|-------------------------|--------------|-------------------------|---------------------------------------|
| Tier 2 Freshwater | 5.9 x 10 ⁻⁷ | 0.0025 | 2.3×10^{-4} | Safe use demonstrated in tier 2 |
| Tier 2 Sediment | 4.75 x 10 ⁻⁷ | 0.002 (EPM) | 2.35 x 10 ⁻⁴ | Safe use demonstrated in tier 2 |
| Tier 2 Marine sediment | 3 x 10 ⁻⁹ | 0.002 (EPM) | 1 x 10 ⁻⁶ | Safe use demonstrated in tier 2 |
| Tier 2 Marine | 8.56 x 10 ⁻⁸ | 0.00025 | 3.4 x 10 ⁻⁵ | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 5, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART

model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 5. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 5 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3, 4, 5, 6 and 7:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|----------------------|---|
| Exposure duration | All | 480 mins |
| Product type | All | Liquid (medium viscosity – like oil) |
| Process temperature | PROC 1,2,3,4 | Hot processes (50-150oC) |
| | PROC 8a,8b, 9,13 | Room temperature (15-25oC) |
| Vapour pressure | All | 6 Pa – Substance is considered to be |
| | | low volatile, exposure to mists is |
| | | estimated |
| Liquid weight fraction | All | 0.98 |
| Primary emission source proximity | PROC 1,2 | Primary emission source is not |
| | | located in the breathing zone of the |
| | | worker - the assessment for this |
| | | activity involves a primary far-field |
| | | emission source only (workers are in |
| | | a control room) |
| | PROC 3,4,8a,8b,9,13 | Primary emission source located in |
| | | the breathing zone of the workers (i.e. |
| | | Within 1 metre) |
| Activity class | PROC 1,2,3,4,8a,8b,9 | Transfer of liquid products |
| | PROC 13 | Activities with open liquid surface or |
| | | reservoirs |
| Containment | PROC 1,2,3,9 | Handling reduces contact between |
| | | product and adjacent air |
| | PROC 4 | Open process, submerged loading |
| | PROC 8a,8b,13 | n/a |
| Localised controls | PROC 1,2,3,8b, | Vapour recovery systems; LEV |
| | PROC 2,4,9 | Vapour recovery |
| | PROC 8a,13 | None |
| Segregation | PROC 1,2 | Complete segregation of workers in |
| | | separate control room |
| Fugative emission source | PROC 1,3,8b,9 | Process fully enclosed – not breached |
| | | for sampling |
| | PROC 2,4,8a,13 | Not fully enclosed – effective |
| | | housekeeping practices in place. |
| Dispersion | PROC 1,2, 8a, 8b | Outdoors not close to buildings |
| | PROC 3,4 | Outdoors near to buildings |
| | PROC 9,13 | Indoors, any sized room, only good |
| | | natural ventilation |

List of derived exposure concentrations

| Description of activity | PROC | Physical | Estimated | Short-term | Estimated | Long-term |
|-------------------------|------|----------------------|---------------------|----------------|---------------------|---------------|
| | | state of material | Exposure (mg/m3) | Concentrations | Exposure (mg/m3) | Concentration |
| | | material | (ing/ind) | | (ing/ints) | |

| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
|--|----|---------|---|---|---|---|
| Use in closed process, no likelihood of exposure | 1 | Liquid | 8.20 x 10 ⁻¹⁰ | 9.30 x 10 ⁻⁰⁹ | 3.60 x 10 ⁻⁰⁹ | 9.40 x 10 ⁻⁰⁹ |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 8.20 x 10 ⁻⁰⁹ | 9.20 x 10 ⁻⁰⁸ | 3.60 x 10 ⁻⁰⁸ | 9.20 x 10 ⁻⁰⁸ |
| Use in closed batch process (synthesis or formulation) | 3 | Liquid | 3.70 x 10 ⁻⁰⁵ | 4.20 x 10 ⁻⁰⁴ | 1.60 x 10 ⁻⁰⁴ | 4.20 x 10 ⁻⁰⁴ |
| Use in batch and other process (synthesis) where opportunity for exposure arises | 4 | Liquid | 0.0012 | 0.014 | 0.0054 | 0.014 |
| Loading/transfer: Loading and unloading a tanker (non- dedicated site) | 8a | Liquid | 0.002 | 0.023 | 0.0088 | 0.023 |
| Loading/transfer: Loading and unloading a tanker (dedicated site) | 8b | Liquid | 1.10 x 10 ⁻⁰⁵ | 1.20 x 10 ⁻⁰⁴ | 4.80 x 10 ⁻⁰⁵ | 4.80 x 10 ⁻⁰⁶ |
| Loading/transfer (filling small containers with sulphuric acid) | 9 | Liquid | 0.00081 | 0.0032 | 0.0011 | 0.0028 |
| Treatment of articles by dipping and pouring (immersion operations) | 13 | Liquids | 0.0045 | 0.018 | 0.0062 | 0.016 |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 5- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|---------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.3 x 10 ⁻⁸ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |
| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 4.2 x 10 ⁻³ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻¹ |
| | | PROC 8b | 1.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.2 x 10 ⁻³ |



| | CES 6 | PROC 9 | 3.2 x 10 ⁻³ | Respiratory | 0.1 | 3.2 x 10 ⁻² |
|------------------------------|-------|---------|------------------------|--|------|------------------------|
| | | | | irritation and corrositivity | | |
| | CES 7 | PROC 13 | 1.8 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.8 x 10 ⁻¹ |
| Long-term – local effects | CES 2 | PROC 1 | 9.4 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |
| | CES 4 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 4.6 x 10 ⁻¹ |
| | | PROC 4 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 5.6 x 10 ⁻² |
| | | PROC 8b | 4.8 x 10 ⁻⁶ | Respiratory irritation and corrositivity | 0.05 | 3.2 x 10 ⁻¹ |
| | CES 6 | PROC 9 | 2.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | CES 7 | PROC 13 | 1.6 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

| 5.4 | Guidance to DU to evaluate whether he works inside the boundaries set by the ES |
|-----|---|
|-----|---|

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 27.4 kg per day
- No emission to the municipal STP

- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Exhaust gases from the intermediate use are treated with scrubbers.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area
- Workers should be segregated from the area of use.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 5.5 Additional good practice advice beyond the REACH CSA. | |
|---|---|
| Alwa surfa Work acid t | ot eat, drink or smoke when working with sulphuric acid. Tys wash hands and exposed skin thoroughly after using sulphuric acid or any ces/machinery that may have come into contact with sulphuric acid. Kers should be suitably trained in all safety procedures and in the safe handling of sulphuric to prevent risk of exposure. PE should be properly maintained and stored in an appropriate way so as not to damage its |

- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

Exposure Scenario 6: Use of Sulphuric Acid in electrolytic processes.

Use of Sulphuric Acid in electrolytic processes.

Processes Covered:

6

Environmental Releases

ERC05: Industrial use resulting in inclusion into or onto a matrix ERC6b: Industrial use of reactive processing aids

Worker Processes

PROC01: Use in closed process, no likelihood of exposure

PROC02: Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance)

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC09: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

PROC13: Treatment of articles by dipping and pouring

Produce Category

PC14: Metal surface treatment products, including galvanic and electroplating products

PC20: Products such as ph-regulators, flocculants, precipitants, neutralization agents

The use of sulphuric acid in electrolytic processes includes metal refining, electroplating of zinc and electrogalvanizing of iron and steel. The processes which use sulphuric acid as electrolytic agents are highly specialised and are controlled to limit emissions and environmental exposure. The electrolytic processes take place in a specially constructed vessel which contains a bath of sulphuric acid solution. Two electrical poles are located either side of the acid bath and these pass current through the electrolyte to achieve electrolysis. As the sulphuric acid acts primarily as an electrolyte the acid may be re-used several times before it is considered spent and sent to the waste system.

Because of the nature of the process during electrolysis (including the corrosive nature of the acid and the electrical currents) specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in electrolytic processes. (ERC 5 and ERC 6B).

Contributing Worker Scenarios: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due transfer of substances to large vessels at dedicated facilities (PROC 8b), CES 5: worker exposure arising due to transfer of formulation to small containers (PROC 9) and CES 6: worker exposure arising due to treatment of articles by dipping and pouring (PROC 13).

6.1

Controlling environmental exposure for ES 6

ES6: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in electrolytic processes.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in electrolytic processes. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid in surface treatment, purification and etching is generally continuous with constant production and use. Facilities generally use between 50 and 200 tonnes per day, with utilization of 2,306 tonnes per year at one site considered to be a worst case assumption.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 50 and 200 tonnes per day in a working year of 365 days, with utilization of 2,306 tonnes per year at one site considered to be a worst case assumption.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 3,160 kg/d but are generally much less. Exhaust gases may be treated by scrubbers.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in electrolysis processes takes place in a highly specialized, high integrity, contained indoor facilities with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used in electrolysis processes on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste waters are generally treated on site by chemical and/or biological methods before release to the municipal STP or to the environment.

Conditions and measures related to external treatment of waste for disposal

All sludge from onsite WWTP is collected and processed for metal recovery, incinerated or sent to landfill. Waste from any scrubbers should be directed to waste water stream for further treatment. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

6.2 Controlling worker exposure for ES 6

ES 6: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 4: worker exposure arising due transfer of substances to large vessels at dedicated facilities (PROC 8b), CES 5: worker exposure arising due to transfer of formulation to small containers (PROC 9) and CES 6: worker exposure arising due to treatment of articles by dipping and pouring (PROC 13).

During the use of sulphuric acid in electrolysis processes, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of tankers with sulphuric acid for use as a surface treatment and etching agent is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use between 50 and 200 tonnes per year in a working year of 365 days, with utilization of 2,306 tonnes per year at one site considered to be a worst case assumption.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance and dipping and pouring are expected to be of a short duration.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with LEV and vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered) in the areas where sulphuric acid is used in electrolytic processes. During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in sampling and transfer of materials to road tankers are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

6.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| ERC 6B Freshwater (in mg/L) | 1.36 x 10 ⁻⁷ | |
| | | |
| ERC 6B Marine water (in mg/L) | 1.97 x 10 ⁻⁸ | |
| ERC 6B Intermittent releases to water (in | NA | Intermittent release not relevant |
| mg/L) | 7 | |
| ERC 6B Freshwater sediment (in mg/kg) | 1.17 x 10 ⁻⁷ | |
| ERC 6B Marine sediment (in mg/kg) | 1.59 x 10 ⁻⁸ | |
| ERC 6B Agricultural soil (averaged over | 9.08 x 10 ⁻⁶ | |
| 30 days (in mg/kg) | | |
| ERC 6B Groundwater (in mg/L) | 6.72 x 10 ⁻⁵ | |
| ERC 6B Annual average PEC in air, total | 1.76 x 10 ⁻³ | |
| (mg/m^3) | | |
| ERC 5 Freshwater (in mg/L) | 6.81 x 10 ⁻⁵ | |
| ERC 5 Marine water (in mg/L) | 9.87 x 10 ⁻⁶ | |
| ERC 5 Intermittent releases to water (in | NA | Intermittent release not relevant |
| mg/L) | | |
| ERC 5 Freshwater sediment (in mg/kg) | 5.48 x 10 ⁻⁵ | |
| ERC 5 Marine sediment (in mg/kg) | 7.94 x 10 ⁻⁶ | |
| ERC 5 Agricultural soil (averaged over 30 | 4.54 x 10 ⁻³ | |
| days (in mg/kg) | | |
| ERC 5 Groundwater (in mg/L) | 0.0336 | |
| ERC 5 Annual average PEC in air, total | 0.878 | |
| (mg/m^3) | | |

The following RCRs were derived taking into account derived PNEC values

| (| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|---|-----------------------------|-------------------------|--------------|------------------------|---------------------------------------|
| | ERC 6B Tier 2 Freshwater | 1.36 x 10 ⁻⁷ | 0.0025 | 5.2 x 10 ⁻⁵ | Safe use demonstrated in tier 2 |

| ERC 6B Tier 2 Sediment | 1.17 x 10 ⁻⁷ | 0.002 (EPM) | 5.5 x 10 ⁻⁵ | Safe use demonstrated in tier 2 |
|----------------------------------|-------------------------|-------------|------------------------|---------------------------------------|
| ERC 6B Tier 2 Marine sediment | 1.59 x 10 ⁻⁸ | 0.002 (EPM) | 7.9 x 10 ⁻⁶ | Safe use demonstrated in tier 2 |
| ERC 6B Tier 2 Marine | 1.97 x 10 ⁻⁸ | 0.00025 | 3.8 x 10 ⁻⁴ | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Freshwater | 6.81 x 10 ⁻⁵ | 0.0025 | 0.039 | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Sediment | 4.48 x 10 ⁻⁵ | 0.002 (EPM) | 0.022 | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Marine sediment | 7.94 x 10 ⁻⁶ | 0.002 (EPM) | 3.9 x 10 ⁻³ | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Marine | 9.87 x 10 ⁻⁶ | 0.00025 | 0.039 | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 6, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 6. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 6 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3, 4, 5 and 6:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-------------------|------|--------------------------------------|
| Exposure duration | All | 480 mins |
| Product type | All | Liquid (medium viscosity – like oil) |

| Process temperature | PROC 1,2 | Hot processes (50-150oC) |
|-----------------------------------|------------------|--|
| | PROC 8b, 9,13 | Room temperature (15-25oC) |
| Vapour pressure | All | 6 Pa – Substance is considered to be low volatile, exposure to mists is estimated |
| Liquid weight fraction | All | 0.98 |
| Primary emission source proximity | PROC 1,2 | Primary emission source is not located in the breathing zone of the worker - the assessment for this activity involves a primary far-field emission source only (workers are in a control room) |
| | PROC,8b,9,13 | Primary emission source located in the breathing zone of the workers (i.e. Within 1 metre) |
| Activity class | PROC 1,2,8b,9 | Transfer of liquid products |
| | PROC 13 | Activities with open liquid surface or reservoirs |
| Containment | PROC 1,2,9 | Handling reduces contact between product and adjacent air |
| | PROC 8b,13 | n/a |
| Localised controls | PROC 1,8b, | Vapour recovery systems; LEV |
| | PROC 2,9 | Vapour recovery |
| | PROC 13 | LE |
| Segregation | PROC 1,2 | Complete segregation of workers in separate control room |
| Fugitive emission source | PROC 1,8b,9 | Process fully enclosed – not breached for sampling |
| | PROC 2,13 | Not fully enclosed – effective housekeeping practices in place. |
| Dispersion | PROC 1,2, 8a, 8b | Outdoors not close to buildings |
| | PROC 9,13 | Indoors, any sized room, only good natural ventilation (however LEV will be employed when needed). |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed process, no likelihood of exposure | 1 | Liquid | 8.20 x 10 ⁻¹⁰ | 9.30 x 10 ⁻⁰⁹ | 3.60 x 10 ⁻⁰⁹ | 9.40 x 10 ⁻⁰⁹ |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 8.20 x 10 ⁻⁰⁹ | 9.20 x 10 ⁻⁰⁸ | 3.60 x 10 ⁻⁰⁸ | 9.20 x 10 ⁻⁰⁸ |
| Loading/transfer: Loading and unloading a tanker (dedicated site) | 8b | Liquid | 1.10 x 10 ⁻⁰⁵ | 1.20 x 10 ⁻⁰⁴ | 4.80 x 10 ⁻⁰⁵ | 4.80 x 10 ⁻⁰⁶ |
| Loading/transfer (filling small containers with | 9 | Liquid | 0.00081 | 0.0032 | 0.0011 | 0.0028 |

| Γ | sulphuric acid) | | | | | | |
|---|--------------------------|----|---------|------|------|------|------|
| | Treatment of articles by | 13 | Liquids | 0.14 | 0.54 | 0.19 | 0.47 |
| | dipping and pouring | | | | | | |
| | (immersion operations) | | | | | | |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 6- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|---|---|-----------------|--|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.3 x 10 ⁻⁸ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |
| | CES 4 | PROC 8b | 1.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.2 x 10 ⁻³ |
| | CES 5 | PROC 9 | 3.2×10^{-3} | Respiratory irritation and corrositivity | 0.1 | 3.2 x10 ⁻² |
| | CES 6 | PROC 13 | $5.4 \times 10^{-1} \\ (3 \times 10^{-2})^*$ | Respiratory irritation and corrositivity | 0.1 | 5.4 x 10 ⁻⁰ (3 x 10 ⁻¹)* |
| Long-term – local effects | CES 2 | PROC 1 | 9.4 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 1.9 x 10 ⁻⁷ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 1.8 x 10 ⁻⁶ |
| | CES 4 | PROC 8b | 4.8 x 10 ⁻⁶ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |
| | CES 5 | PROC 9 | 2.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 5.6 x 10 ⁻² |
| | CES 6 | PROC 13 | $\begin{array}{c} 4.7 \text{ x } 10^{-1} \\ (2 \text{ x } 10^{-2})^* \end{array}$ | Respiratory irritation and corrositivity | 0.05 | 9.4 x 10^{-0} (4 x 10^{-1})* |

* Assumes Respiratory Protective Equipment (95% reduction) is worn

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

| 6.4 | | |
|-----|--|--|

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 3,160 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Exhaust gases from the intermediate use are treated with scrubbers.
- Sufficient LEV and vapour recovery systems are in place to reduce exposure when open electrolyte baths are in place..
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area
- Workers should be segregated from the area of use.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

6.5

Additional good practice advice beyond the REACH CSA.

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

7 Exposure Scenario 7: Use of Sulphuric Acid in gas purification, scrubbing, flue gas scrubbing etching.

Use of Sulphuric Acid in gas purification, scrubbing, flue gas scrubbing etching.

Processes Covered:

Environmental Releases

ERC07: Industrial use of substances in closed systems

Worker Processes

PROC01: Use in closed process, no likelihood of exposure

PROC02: Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance)

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

Produce Category

PC20: Products such as ph-regulators, flocculants, precipitants, neutralization agents

Sulphuric acid as may be used as an agent for gas purification. This includes gas scrubbing and flue gas scrubbing. The main applications of this would be in purification of gas from coke ovens and in the purification and drying of industrial gases generated from the manufacture of other substances.

Due to the corrosive nature of sulphuric acid, specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in gas purification, scrubbing, flue gas scrubbing etching. (ERC 7).

Contributing Worker Scenarios: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), and CES 4: worker exposure arising due transfer of substances to large vessels at dedicated facilities (PROC 8b).

7.1 Controlling environmental exposure for ES 7

ES7: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in gas purification, scrubbing, flue gas scrubbing etching.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in gas purification, scrubbing, flue gas scrubbing etching. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant

compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation. In addition to these risk management measures, direct emission of de-contaminated sulphuric acid to surface water exists where around 560 tonnes of sulphuric acid per year is emitted to a large brackish river with a large acid buffering capacity and a very high flow rate.

Use of sulphuric acid in gas purification, scrubbing, flue gas scrubbing etching is generally continuous with constant production and use. Facilities generally use up to 30,000 tonnes per year which is considered to be a worst case assumption for a single site in Europe, with reports of 1.5tonnes emitted per day in some sites.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 30,000 tonnes per year which is considered to be a worst case assumption for a single site in Europe, with reports of 1.5tonnes emitted per day in some sites.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 5,000 kg/d but are generally much less. Exhaust gases may be treated by scrubbers and filtered.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in facilities in the process of gas purification, scrubbing and flue gas scrubbing takes place in a highly specialized, high integrity, contained indoor facilities with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems, with insulation if required.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed and insulated if necessary. Both production and sampling are carried out in dedicated facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used in the process of gas purification, scrubbing and flue gas scrubbing on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. Spent acid solutions are neutralized to circumneutral pH prior to discharge. All waste waters should be treated in this manner.

In some cases, emissions are made to a large brackish river with a considerable buffering capacity and a very high flow rate.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste waters are generally treated on site by chemical and/or biological methods before release to the municipal STP or to the environment.

Conditions and measures related to external treatment of waste for disposal

All sludge from the onsite WWTP is collected and incinerated or sent to landfill for disposal. Waste from any scrubbers should be directed to waste water stream for further treatment. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

7.2

Controlling worker exposure for ES 7

ES 7: CES 2: Worker exposure arising due to use in closed processes with no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2) and CES 4: worker exposure arising due transfer of substances to large vessels at dedicated facilities (PROC 8b).

During the use of sulphuric acid in the process of gas purification, scrubbing and flue gas scrubbing, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of tankers with sulphuric acid to be used as a gas purifier is usually performed in semi-closed conditions. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 30,000 tonnes per year, considered to be 365 days, which is considered to be a worst case assumption for a single site in Europe, with reports of 1.5tonnes emitted per day in some sites.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance are expected to be short duration tasks. Human factors not influenced by risk management

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and

/or filtered) in the areas where sulphuric acid is used in electrolytic processes. During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in sampling and transfer of materials to road tankers are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks. Workers are generally separated from the purification or scrubbing systems with no direct contact to the installations housing the material.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

7.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|--|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 8.86 x 10 ⁻⁵ | |
| Marine water (in mg/L) | 1.28 x 10 ⁻⁵ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 7.13 x 10 ⁻⁵ | |
| Marine sediment (in mg/kg) | 1.03 x 10 ⁻⁵ | |
| Agricultural soil (averaged over 30 days (in mg/kg) | 5.91 x 10 ⁻³ | |
| Groundwater (in mg/L) | 0.0437 | |
| Annual average PEC in air, total (mg/m ³) | 1.14 | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|-------------------|-------------------------|--------------|----------|---------------------------------------|
| Tier 2 Freshwater | 8.86 x 10 ⁻⁵ | 0.0025 | 0.0352 | Safe use demonstrated in tier 2 |
| Tier 2 Sediment | 7.13 x 10 ⁻⁵ | 0.002 (EPM) | 0.0355 | Safe use demonstrated in tier 2 |

| Tier 2 Marine sediment | 1.03 x 10 ⁻⁵ | 0.002 (EPM) | 0.005 | Safe use demonstrated in tier 2 |
|---------------------------|-------------------------|-------------|-------|---------------------------------------|
| Tier 2 Marine | 1.28 x 10 ⁻⁵ | 0.00025 | 0.048 | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 7, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 7. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 7 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3 and 4:

| | PROC | Parameters/ assumptions | |
|-----------------------------------|------------|---|--|
| Exposure duration | All | 480 mins | |
| Product type | All | Liquid (medium viscosity – like oil | |
| Process temperature | All | Hot processes (50-150oC) | |
| Vapour pressure | All | 6 Pa – Substance is considered to be | |
| | | low-volatile, exposure to mists is | |
| | | estimated | |
| Liquid weight fraction | All | 0.98 | |
| Primary emission source proximity | PROC 1,2 | Primary emission source is not | |
| | | located in the breathing zone of the | |
| | | worker - the assessment for this | |
| | | activity involves a primary far-field | |
| | | emission source only (workers are in | |
| | | a control room) | |
| | PROC 8b | Primary emission source located in | |
| | | the breathing zone of the workers (i.e. | |
| | | Within 1 metre) | |
| Activity class | All | Transfer of liquid products | |
| Containment | PROC 1,2, | Handling reduces contact between | |
| | | product and adjacent air | |
| | PROC 8b | n/a | |
| Localised controls | PROC 1,8b, | Vapour recovery systems; LEV | |

List of inputs used in the ART assessment

| | PROC 2 | Vapour recovery |
|--------------------------|-------------|---------------------------------------|
| Segregation | PROC 1,2 | Complete segregation of workers in |
| | | separate control room |
| Fugitive emission source | PROC 1,8b | Process fully enclosed – not breached |
| | | for sampling |
| | PROC 2 | Not fully enclosed – effective |
| | | housekeeping practices in place. |
| Dispersion | PROC 1,2,8b | Outdoors not close to buildings |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed process, no likelihood of exposure | 1 | Liquid | 8.20 x 10 ⁻¹⁰ | 9.30 x 10 ⁻⁰⁹ | 3.60 x 10 ⁻⁰⁹ | 9.40 x 10 ⁻⁰⁹ |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 8.20 x 10 ⁻⁰⁹ | 9.20 x 10 ⁻⁰⁸ | 3.60 x 10 ⁻⁰⁸ | 9.20 x 10 ⁻⁰⁸ |
| Loading/transfer of sulphuric acid to/from large vessels/containers at dedicated site | 8b | Liquid | 1.10 x 10 ⁻⁰⁵ | 1.20 x 10 ⁻⁰⁴ | 4.80 x 10 ⁻⁰⁵ | 4.80 x 10 ⁻⁰⁶ |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 7- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.3 x 10 ⁻⁸ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.1 | 9.2 x 10 ⁻⁷ |
| | CES 4 | PROC 8b | 1.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.2 x 10 ⁻³ |
| Long-term – local effects | CES 2 | PROC 1 | 9.4 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 1.88 x 10 ⁻⁷ |
| | CES 3 | PROC 2 | 9.2 x 10 ⁻⁸ | Respiratory irritation and corrositivity | 0.05 | 1.84 x 10 ⁻⁶ |
| | CES 4 | PROC 8b | 4.8 x 10 ⁻⁶ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |



Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for

exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

7.4 Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 5,000 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Exhaust gases from use are treated with scrubbers.
- Sufficient vapour recovery systems are in place to reduce exposure.
- In some instances, emissions are released to large brackish lakes with a very high acid buffering capacity and high flow rate.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area
- Workers should be segregated from the area of use.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 7.5 | Additional good practice advice beyond the REACH CSA. |
|--|---|
| Alwa surfa Worl acid All F integ | ot eat, drink or smoke when working with sulphuric acid. Ays wash hands and exposed skin thoroughly after using sulphuric acid or any aces/machinery that may have come into contact with sulphuric acid. Kers should be suitably trained in all safety procedures and in the safe handling of sulphuric to prevent risk of exposure. PPE should be properly maintained and stored in an appropriate way so as not to damage its grity. Workers should be correctly trained in its use. |

• Procedural and safety compliance should be routinely assessed by management

- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

Exposure Scenario 8: Use of Sulphuric Acid in production of lead acid batteries containing sulphuric acid.

Use of Sulphuric Acid in production of lead acid batteries containing sulphuric acid.

Processes Covered:

8

Environmental Releases

ERC02: Formulation of preparations ERC05: Industrial use resulting in inclusion into or onto a matrix

Worker Processes

PROC02: Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance)

PROC03: Use in closed batch process (synthesis or formulation)

PROC04: Use in batch and other process (synthesis) where opportunity for exposure arises PROC09: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

Produce Category

PC0: Other [UNC code E10100 (Electrolytes)]

Sulphuric acid is used in the production of the liquid electrolyte for batteries. The electrolyte solution generally contains sulphuric acid at a concentration of 25% to 40%. The electrolyte solution is added to the batteries and then sealed within them.

Because of the processes involved in battery manufacturing (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in the production of lead acid batteries containing sulphuric acid. (ERC 02 and ERC 05).

Contributing Worker Scenarios: CES 2: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 3: worker exposure arising due to use in batch processes with some potential for exposure (PROC 3 and PROC 4), and CES 4: worker exposure arising due transfer of formulations or preparations to small containers (PROC 9).

Controlling environmental exposure for ES 8

ES8: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in production of lead acid batteries containing sulphuric acid.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in production of lead acid batteries containing sulphuric acid. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water. Sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid in the production of lead acid batteries containing sulphuric acid is generally continuous with constant production and use. Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 12,500 kg/d but are generally much less. Exhaust gases may be treated by scrubbers and filtered.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in the production of lead acid batteries containing sulphuric acid takes place in a highly specialized, high integrity, contained indoor facilities with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems, with insulation if required.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed and insulated if necessary. Both production and sampling are carried out in dedicated, contained facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used in the production of lead acid batteries containing sulphuric acid on a large scale generally occurs on major chemical sites which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste waters are generally treated on site by chemical and/or biological methods before release to the municipal STP or to the environment.

Conditions and measures related to external treatment of waste for disposal

All sludge from the onsite WWTP is collected and incinerated or sent to landfill for disposal. Waste from any scrubbers should be directed to waste water stream for further treatment. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

8.2

Controlling worker exposure for ES 8

ES 8: CES 2: worker exposure arising due to use in closed processes with some potential for exposure (PROC 2), CES 3: worker exposure arising due to use in batch processes with some potential for exposure (PROC 3 and PROC 4), and CES 4: worker exposure arising due transfer of formulations or preparations to small containers (PROC 9).

During the use of sulphuric acid in the production of lead acid batteries containing sulphuric acid, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of tankers with sulphuric acid for use in battery manufacture is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). Where required, respiratory protection is also provided. A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover. Filling of the batteries would generally be indoors with suitable LEV and worker protection measures in place.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, some tasks, such as sampling and maintenance are expected to be short duration tasks. Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Both production and sampling are carried out at dedicated facilities with LEV and vapour recovery systems in place where required. Transfer operations are carried out in controlled systems with dedicated machinery. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems. Loss from reactor and pipes is monitored.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered) in the areas where sulphuric acid is used in electrolytic processes. During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in sampling and transfer of materials to road tankers are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks. Workers are generally separated from the machinery associated with sulphuric acid, with no direct contact to the installations housing the material. During the short duration tasks where exposure is possible, suitable PPE is worn.

Conditions and measures related to personal protection, hygiene and health.

Gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure. Respiratory equipment may also be worn if necessary.

8.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| ERC 2 Freshwater (in mg/L) | 3.69 x 10 ⁻⁵ | |
| | | |
| ERC 2 Marine water (in mg/L) | 5.35 x 10 ⁻⁶ | |
| ERC 2 Intermittent releases to water (in | NA | Intermittent release not relevant |
| mg/L) | | |
| ERC 2 Freshwater sediment (in mg/kg) | 2.97 x 10 ⁻⁵ | |
| ERC 2 Marine sediment (in mg/kg) | 4.3 x 10 ⁻⁶ | |
| ERC 2 Agricultural soil (averaged over 30 | 2.46 x 10 ⁻⁴ | |
| days (in mg/kg) | | |
| ERC 2 Groundwater (in mg/L) | 1.82×10^{-3} | |
| ERC 2 Annual average PEC in air, total | 0.0476 | |
| (mg/m^3) | | |
| ERC 5 Freshwater (in mg/L) | 7.38 x 10 ⁻⁵ | |
| ERC 5 Marine water (in mg/L) | 1.07 x 10 ⁻⁵ | 10-fold dilution by receiving |
| | | waters. |
| ERC 5 Intermittent releases to water (in | NA | Intermittent release not relevant |
| mg/L) | | |

| ERC 5 Freshwater sediment (in mg/kg) | 5.94×10^{-5} | |
|---|-------------------------|--|
| ERC 5 Marine sediment (in mg/kg) | 8.8 x 10 ⁻⁶ | |
| ERC 5 Agricultural soil (averaged over 30 | 4.92 x 10 ⁻³ | |
| days (in mg/kg) | | |
| ERC 5 Groundwater (in mg/L) | 0.0364 | |
| ERC 5 Annual average PEC in air, total | 0.952 | |
| (mg/m^3) | | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|------------------------------|-------------------------|--------------|----------|---------------------------------------|
| ERC 2 Tier 2 Freshwater | 3.69 x 10 ⁻⁵ | 0.0025 | 0.0147 | Safe use demonstrated in tier 2 |
| ERC 2 Tier 2 Sediment | 2.97 x 10 ⁻⁵ | 0.002 (EPM) | 0.0148 | Safe use demonstrated in tier 2 |
| ERC 2 Tier 2 Marine sediment | 4.3 x 10 ⁻⁶ | 0.002 (EPM) | 0.0021 | Safe use demonstrated in tier 2 |
| ERC 2 Tier 2 Marine | 5.35 x 10 ⁻⁶ | 0.00025 | 0.0212 | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Freshwater | 7.38 x 10 ⁻⁵ | 0.0025 | 0.0295 | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Sediment | 5.94 x 10 ⁻⁵ | 0.002 (EPM) | 0.029 | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Marine sediment | 8.8 x 10 ⁻⁶ | 0.002 (EPM) | 0.0044 | Safe use demonstrated in tier 2 |
| ERC 5Tier 2 Marine | 1.07 x 10 ⁻⁵ | 0.00025 | 0.042 | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 8, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 8. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 8 do not pose an unacceptable health risk to workers.

Information for worker contributing scenarios 2, 3 and 4:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions | |
|-----------------------------------|------------|--|--|
| Exposure duration | All | 480 mins | |
| Product type | PROC 2,3 | Liquid (medium viscosity – like oil) | |
| | PROC 4,9 | Liquid (low viscosity – like water) | |
| Process temperature | All | Room temperature (15-25oC) | |
| Vapour pressure | All | Substance is considered to be low volatile, exposure to mists is estimated | |
| Liquid weight fraction | PROC 2,3 | 0.98 | |
| | PROC 4,9 | 0.25 | |
| Primary emission source proximity | All | Primary emission source located in the breathing zone of the workers (i.e. Within 1 metre) | |
| Activity class | All | Transfer of liquid products | |
| Containment | All | Handling reduces contact between product and adjacent air | |
| Localised controls | All | LEV | |
| Fugitive emission source | PROC 2 | Process fully enclosed – not breached for sampling | |
| | PROC 3,4,9 | Not fully enclosed – effective housekeeping practices in place. | |
| Dispersion | All | Indoors, any sized room, only good natural ventilation | |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 4.00 x 10 ⁻⁰⁴ | 1.60 x 10 ⁻⁰³ | 5.50 x 10 ⁻⁰⁴ | 1.40 x 10 ⁻⁰³ |
| Use in closed batch process (synthesis or formulation) | 3 | Liquid | 0.0041 | 0.016 | 0.0056 | 0.014 |
| Use in batch and other process (synthesis) where opportunity for exposure arises | 4 | Liquid | 0.00034 | 0.0014 | 0.00048 | 0.0012 |
| Loading/transfer (small containers): Filling lead-acid | 9 | Liquid | 0.00034 | 0.0014 | 0.00048 | 0.0012 |

| - | | | | |
|---|-------------------------------|--|--|--|
| | batteries with sulphuric acid | | | |
| | electrolyte, diluted 25% | | | |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 8- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 2 | 1.6 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 1.6 x 10 ⁻² |
| | CES 3 | PROC 3 | 1.6 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.6 x 10 ⁻¹ |
| | | PROC 4 | 1.4 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻² |
| | CES 4 | PROC 9 | 1.4 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻² |
| Long-term – local effects | CES 2 | PROC 2 | 1.4 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻² |
| | CES 3 | PROC 3 | 1.4 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 2.8 x 10 ⁻¹ |
| | | PROC 4 | 1.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 2.4×10^{-2} |
| | CES 4 | PROC 9 | 1.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 2.4×10^{-2} |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems

and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

| 8.4 | Guidance to DU to evaluate whether he works inside the boundaries set by the ES |
|-----|---|
|-----|---|

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 12,500 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil

- Wastewater should be fully neutralized
- Exhaust gases from use are treated with scrubbers.
- Sufficient LEV and vapour recovery systems are in place to reduce exposure.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective gloves, goggles, overalls and boots at all times in the production and transfer area.
- Respiratory protection should be worn when required.
- Workers should be segregated from the area of use with no direct contact with the installation housing the machinery.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 8.5 | Additional good practice advice beyond the REACH CSA. | | | | | |
|-----|--|--|--|--|--|--|
| | ot eat, drink or smoke when working with sulphuric acid. ays wash hands and exposed skin thoroughly after using sulphuric acid or any | | | | | |

- surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

| 9 | Exposure Scenario 9: Use of sulphuric acid in maintenance of sulphuric acid contained |
|---|---|
| | batteries. |

Use of sulphuric acid in maintenance of sulphuric acid contained batteries

Processes Covered:

Environmental Releases

ERC08b: Wide dispersive indoor use of reactive substances in open systems ERC09b: Wide dispersive outdoor use of substances in closed systems

Worker Processes

PROC19: Hand-mixing with intimate contact and only PPE available

Produce Category

PC0: Other [UNC code E10100 (Electrolytes)]

Sulphuric acid may be involved in battery maintenance. Given that batteries are sealed articles and that the sulphuric acid involved in their maintenance is not intended for direct release, exposure to and emission from sulphuric acid in these processes should be minimal. The only exposure from the maintenance of lead acid batteries will come when the electrolyte solution is topped off or replaced with fresh de-ionized water.

Because of the processes involved in battery maintenance (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in the maintenance of sulphuric acid contained batteries. (ERC 08b and ERC 09b).

Contributing Worker Scenarios: CES 2: worker exposure arising due to hand-mixing with intimate contact and only PPE available (PROC 19).

9.1

Controlling environmental exposure for ES 9

ES9: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in the maintenance of sulphuric acid contained batteries.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in the maintenance of sulphuric acid contained batteries. These releases may potentially occur due to emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and filtered, significantly lessening the possible emission by atmospheric deposition to soil or surface waters.

Waste stream treatment may also be employed to reduce environmental exposure however for this wide dispersive use particular risk management measures are not needed to demonstrate environmental safe use.

Use of sulphuric acid in the maintenance of sulphuric acid contained batteries is generally continuous with constant production and use. Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption

for a single site in Europe, operating 365 days per year.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 34.2 kg/d but are generally much less. Exhaust gases may be treated by scrubbers and filtered.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in the maintenance of sulphuric acid contained batteries takes place in outdoor facilities. Any gas displaced from containers is conducted via pipeline to be processed i.e. removed and scrubbed and /or filtered. Reactors and transfer pipelines are closed systems, with insulation if required.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed and insulated if necessary. Both production and sampling are carried out in dedicated, contained facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid used in the maintenance of sulphuric acid contained batteries on a large scale generally is only required on a rare occurrence. However, in the event that it is required, waste stream treatment may be employed to reduce environmental exposure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

There is no release to the municipal STP due to the rare occurrence of the activity described in this exposure scenario.

Conditions and measures related to external treatment of waste for disposal

There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

9.2 Controllin

Controlling worker exposure for ES 9

ES 9: CES 2: worker exposure arising due to hand-mixing with intimate contact and only PPE available (PROC 19).

During the use of sulphuric acid in the maintenance of sulphuric acid contained batteries, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of vessels of sulphuric acid for use in maintenance of batteries is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover. Any gas displaced from containers is conducted via pipeline to be processed i.e. removed and scrubbed and /or filtered.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, the activities associated with this exposure scenario generally only occur rarely.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Maintenance of batteries is generally carried out by trained technicians in facilities with exposure and waste treatment procedures in place. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure.

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered).

Organizational measures to prevent/limit release

Workers involved in loading and unloading of vessels of sulphuric acid for use in maintenance of batteries wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage.

Conditions and measures related to personal protection, hygiene and health.

Anti-acid gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

9.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| ERC 8B Freshwater (in mg/L) | 3.31 x 10 ⁻⁵ | |
| ERC 8B Marine water (in mg/L) | 2.29 x 10 ⁻⁵ | |
| ERC 8B Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| ERC 8B Freshwater sediment (in mg/kg) | 2.67 x 10 ⁻⁵ | |
| ERC 8B Marine sediment (in mg/kg) | 1.84 x 10 ⁻⁵ | |

| | Ē | |
|---|-------------------------|-----------------------------------|
| ERC 8B Agricultural soil (averaged over | 5.77 x 10 ⁻⁵ | |
| 30 days (in mg/kg) | | |
| ERC 8B Groundwater (in mg/L) | 9.08 x 10 ⁻⁵ | |
| ERC 8B Annual average PEC in air, total | 1.9 x 10 ⁻⁴ | |
| (mg/m^3) | | |
| ERC 9B Freshwater (in mg/L) | 8.99 x 10 ⁻⁵ | |
| ERC 9B Marine water (in mg/L) | 5.83 x 10 ⁻⁵ | |
| ERC 9B Intermittent releases to water (in | NA | Intermittent release not relevant |
| mg/L) | | |
| ERC 9B Freshwater sediment (in mg/kg) | 7.23 x 10 ⁻⁵ | |
| ERC 9B Marine sediment (in mg/kg) | 4.69 x 10 ⁻⁵ | |
| ERC 9B Agricultural soil (averaged over | 2.96 x 10 ⁻⁴ | |
| 30 days (in mg/kg) | | |
| ERC 9B Groundwater (in mg/L) | 1.35 x 10 ⁻³ | |
| ERC 9B Annual average PEC in air, total | 9.52 x 10 ⁻³ | |
| (mg/m^3) | | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|----------------------------------|-------------------------|--------------|----------|---|
| ERC 8B Tier 1 Freshwater | 2.26 x 10 ⁻⁵ | 0.0025 | 0.009 | Safe use in tier 1 for all compartments |
| ERC 8B Tier 1 Sediment | 2.67 x 10 ⁻⁵ | 0.002 (EPM) | 0.0133 | |
| ERC 8B Tier 1 Marine sediment | 1.84 x 10 ⁻⁵ | 0.002 (EPM) | 0.009 | |
| ERC 8B Tier 1 Marine | 2.26 x 10 ⁻⁵ | 0.00025 | 0.09 | |
| ERC 9B Tier 1 Freshwater | 5.64 x 10 ⁻⁵ | 0.0025 | 0.02 | Safe use in tier 1 for all compartments |
| ERC 9BTier 1 Sediment | 1.84 x 10 ⁻⁵ | 0.002 (EPM) | 0.0092 | |
| ERC 9BTier 1 Marine sediment | 4.69 x 10 ⁻⁵ | 0.002 (EPM) | 0.0023 | |
| ERC 9BTier 1 Marine | 5.64 x 10 ⁻⁵ | 0.00025 | 0.22 | |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 9, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table

below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 9. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 9 do not pose an unacceptable health risk to workers.

Information for worker contributing scenario 2:

| | PROC | Parameters/ assumptions |
|-----------------------------------|---------|---|
| Exposure duration | PROC 19 | 240 mins exposure / day; 240 mins |
| - | | non-exposure/day |
| Product type | PROC 19 | Liquid (low viscosity – like water) |
| Process temperature | PROC 19 | Room temperature (15-25oC) |
| Vapour pressure | PROC 19 | Substance is considered to be low |
| | | volatile, exposure to acid mists is |
| | | estimated |
| Liquid weight fraction | PROC 19 | 0.25 |
| Primary emission source proximity | PROC 19 | Primary emission source located in |
| | | the breathing zone of the workers (i.e. |
| | | Within 1 metre) |
| Activity class | PROC 19 | Handling of contaminated objects |
| Localised controls | PROC 19 | None |
| Fugative emission source | PROC 19 | Not fully enclosed – effective |
| - | | housekeeping practices in place |
| Dispersion | PROC 19 | Indoors, any sized room, only good |
| - | | natural ventilation |

List of inputs used in the ART assessment

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|---|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Hand-mixing with intimate contact: only PPE available | 19 | Liquid | 0.00058 | 0.0023 | 0.00079 | 0.002 |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 9- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------|-------|-----------|---|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 19 | 2.3 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻² |

| Long-term – local effects | CES 2 | PROC 19 | 2×10^{-3} | Respiratory irritation and | 0.05 | $4x \ 10^{-2}$ | |
|------------------------------|-------|---------|--------------------|----------------------------|------|----------------|--|
| | | | | corrositivity | | | |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and

boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

9.4

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 34.2 kg per day
- No emission to the municipal STP
- Waste stream treatment may also be employed to reduce environmental exposure.
- Gas displaced from containers is conducted via pipeline to be scrubbed and /or filtered.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective anti-acid gloves, goggles, overalls and boots at all times in the production and transfer area.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

9.5

Additional good practice advice beyond the REACH CSA.

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and

confirmed to be functioning correctly

10 Exposure Scenario 10: Recycling of lead acid batteries containing sulphuric acid

Use of sulphuric acid in maintenance of sulphuric acid contained batteries

Processes Covered:

Environmental Releases

ERC01: Manufacture of Substances

Worker Processes

PROC02: Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance)

PROC04: Use in batch and other process (synthesis) where opportunity for exposure arises

PROC05: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact)

PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

Produce Category

PC0: Other [UNC code E10100 (Electrolytes)]

Sulphuric acid, at a concentration of 25 to 40%, may be involved in the recycling of batteries. The process of battery recycling is aimed at recovery of the lead from the battery plates and removal of the sulphuric acid electrolyte solution. The batteries are mechanically crushed using, for example, a hydraulic press, and the electrolyte is drained and collected. Recovered acid may be re-used for some applications or can be neutralized and treated to remove contaminants and disposed.

Because of the processes involved in the recycling of batteries (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in the recycling of batteries. (ERC 01).

Contributing Worker Scenarios: CES 2: worker exposure arising due to use in a closed process with occasional controlled exposure (PROC 02), CES 3: worker exposure arising due to use in batch and other processes where opportunity for exposure may arise (PROC 04), CES 4: worker exposure due to mixing or blending in batch processes (PROC 05) and CES 5: worker exposure due to transfer of substance or preparation from/to vessels/large containers at non-dedicated facilities (PROC 8a).

Controlling environmental exposure for ES 10

ES10: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in the recycling of batteries.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in the recycling of batteries. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralisation to neutral pH) prior to emission to remove any sulphuric acid in the waste water and sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid in the recycling of batteries is generally continuous with constant production and use. Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Product characteristics

The produced substance is a liquid with purity between 25 to 40%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 34.2 kg/d but are generally much less. Exhaust gases may be treated by scrubbers and filtered.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in the recycling of batteries takes place in outdoor facilities. Any gas displaced from containers is conducted via pipeline to be processed i.e. removed and scrubbed and /or filtered. Reactors and transfer pipelines are closed systems, with insulation if required.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed and insulated if necessary. Both production and sampling are carried out in dedicated, contained facilities.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Waste waters are generally treated on site by chemical and/or biological methods before release to the municipal STP or to the environment. All sludge is collected and incinerated or sent to landfill. All gas emissions are scrubbed and filtered and may also then be diverted to the wastewater stream.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste waters are generally treated on site by chemical and/or biological methods before release to the municipal STP or to the environment.

Conditions and measures related to external treatment of waste for disposal

All sludge from the onsite WWTP is collected and incinerated or sent to landfill for disposal. Waste from any scrubbers should be directed to waste water stream for further treatment. There is no further generation of solid waste

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

10.2

Controlling worker exposure for ES 10

ES 10: CES 2: worker exposure arising due to use in a closed process with occasional controlled exposure (PROC 02), CES 3: worker exposure arising due to use in batch and other processes where opportunity for exposure may arise (PROC 04), CES 4: worker exposure due to mixing or blending in batch processes (PROC 05) and CES 5: worker exposure due to transfer of substance or preparation from/to vessesl/large containers at non-dedicated facilities (PROC 8a).

During the use of sulphuric acid in the recycling of sulphuric acid batteries, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of vessels of sulphuric acid for use in the recycling of batteries containing is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage.

Gas displacement lines are also used if filling of road tankers takes place under cover. Any gas displaced from containers is conducted via pipeline to be processed i.e. removed and scrubbed and /or filtered.

Product characteristics

The produced substance is a liquid with purity between 25 to 40%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, these activities are expected to be short duration tasks and 8 hours per day is a worst case assumption.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Recycling of batteries is generally carried out by trained technicians in facilities with exposure and waste treatment procedures in place. The handling of sulphuric acid involves special equipment and controlled systems with little or no potential for exposure. Workers involved in the loading and unloading of vessels of sulphuric acid for use in the recycling of batteries is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall).

Technical conditions and measures at process level (source) to prevent release

Reactors and pipes are sealed systems.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is conducted via pipeline to be processed (removed and scrubbed and /or filtered). During handling when transferring drum filling, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in loading and unloading of vessels of sulphuric acid for use in the recycling of batteries wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall) to minimise the risk of exposure.

Conditions and measures related to personal protection, hygiene and health.

Anti-acid gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

10.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 7.38 x 10 ⁻⁶ | |
| Marine water (in mg/L) | 1.07 x 10 ⁻⁶ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 5.94 x 10 ⁻⁶ | |
| Marine sediment (in mg/kg) | 8.6 x 10 ⁻⁷ | |
| Agricultural soil (averaged over 30 days | 1.6 x 10 ⁻⁴ | |
| (in mg/kg) | | |
| Groundwater (in mg/L) | 1.18 x 10 ⁻³ | |
| Annual average PEC in air, total (mg/m ³) | 9.52 x 10 ⁻³ | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|-------------------|-------------------------|--------------|----------|---------------------------------------|
| Tier 2 Freshwater | 7.38 x 10 ⁻⁶ | 0.0025 | 0.00292 | Safe use demonstrated in tier 2 |
| Tier 2 Sediment | 5.94 x 10 ⁻⁶ | 0.002 (EPM) | 0.0029 | Safe use demonstrated in tier 2 |

| Tier 2 Marine sediment | 8.6 x 10 ⁻⁷ | 0.002 (EPM) | 4.3 x 10 ⁻⁴ | Safe use demonstrated in tier 2 |
|---------------------------|-------------------------|-------------|------------------------|---------------------------------------|
| Tier 2 Marine | 1.07 x 10 ⁻⁶ | 0.00025 | 0.0042 | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 10, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 10. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 10 do not pose an unacceptable health risk to workers.

Information for worker contributing scenario 2, 3, 4 and 5:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|--------------|---|
| Exposure duration | All | 480 mins |
| Product type | All | Liquid (low viscosity – like water) |
| Process temperature | All | Room temperature (15-25oC) |
| Vapour pressure | All | Substance is considered to be low |
| | | volatile, exposure to mists is |
| | | estimated |
| Liquid weight fraction | All | 0.25 |
| Primary emission source proximity | All | Primary emission source located in |
| | | the breathing zone of the workers (i.e. |
| | | Within 1 metre) |
| Activity class | PROC 2,4 | Transfer of liquid products |
| | PROC 2,4, 8a | Transfer of liquid products – falling |
| | | liquids, 1-10 L/min |
| | PROC 5 | Activities with open surfaces |
| Containment | PROC 2 | Handling reduces contact between |
| | | product and adjacent air |
| | PROC 8a | Handling reduces contact between |
| | | product and adjacent air – submerged |
| | | loading |
| | PROC 4 | Open process – submerged loading |

| | PROC 5 | n/a |
|--------------------------|--------|------------------------------------|
| Localised controls | All | LEV |
| Fugitive emission source | All | Not fully enclosed – effective |
| | | housekeeping practices in place. |
| Dispersion | All | Indoors, any sized room, only good |
| | | natural ventilation |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|---|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 0.00035 | 0.0014 | 0.00047 | 0.0012 |
| Use in batch and other process (synthesis) where opportunity for exposure arises | 4 | Liquid | 0.0012 | 0.0046 | 0.0016 | 0.004 |
| Mixing or blending in batch process for formulation of preparations or articles (multistage and/or significant contact) | 5 | Liquid | 0.0038 | 0.015 | 0.0053 | 0.013 |
| Transfer of 10% sulphuric acid cleaning solution to/from large vessels/containers at non- dedicated facilities | 8b | Liquid | 0.0017 | 0.0069 | 0.0024 | 0.006 |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 10- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|---------------------|-------|-----------|--|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 02 | 1.4 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 1.4 x 10 ⁻² |
| | CES 3 | PROC 04 | 4.6 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 4.6 x 10 ⁻² |
| | CES 4 | PROC 05 | 1.5 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.5 x 10 ⁻¹ |

| | CES 5 | PROC 08b | 6.9 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 6.9 x 10 ⁻² |
|------------------------------|-------|----------|------------------------|--|------|------------------------|
| Long-term – local effects | CES 2 | PROC 02 | 1.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 2.4×10^{-2} |
| | CES 3 | PROC 04 | 4 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 8 x 10 ⁻² |
| | CES 4 | PROC 05 | 1.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 2.6×10^{-1} |
| | CES 5 | PROC 08b | 6 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 1.2×10^{-1} |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work

practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

10.4

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 34.2 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Waste stream treatment may also be employed to reduce environmental exposure.
- Gas displaced from containers is conducted via pipeline to be scrubbed and /or filtered.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Reactors and pipelines should be sealed systems
- Workers should wear protective anti-acid gloves, goggles, overalls and boots at all times in the production and transfer area.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 10.5 | Additional good practice advice beyond the REACH CSA. |
|------|---|
| | |

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

11 Exposure Scenario 11: Use of lead acid batteries containing sulphuric acid

Use of lead acid batteries containing sulphuric acid.

Processes Covered:

Environmental Releases

ERC09b: Wide dispersive outdoor use of substances in closed systems

Worker Processes

PROC19: Hand-mixing with intimate contact and only PPE available

Article Category

AC3: Electrical batteries and accumulators

Sulphuric acid may be used in battery maintenance in the form of DIY battery maintenance/top-up kits, primarily by consumers. As batteries are sealed articles and that the sulphuric acid involved in their maintenance is not intended for direct release, exposure to and emission from sulphuric acid in these processes should be minimal.

Because of the processes involved in the recycling of batteries (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of lead acid batteries containing sulphuric acid. (ERC 01).

Contributing Worker Scenarios: CES 2: consumer exposure arising due to hand-mixing with intimate contact and only PPE available (PROC 19).

11.1 Controlling environmental exposure for ES 11

ES11: Contributing exposure scenario (CES) 1 Environmental exposure arising due to the use of lead acid batteries containing sulphuric acid.

Section 2.1 describes the environmental releases that may occur during the use of lead acid batteries containing sulphuric acid. Environmental emissions may be limited by waste stream treatment, however for this wide dispersive use particular risk management measures are not needed to demonstrate environmental safe use.

Use of lead acid batteries containing sulphuric acid is generally considered to be a sporadic activity which is not continuous. Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Product characteristics

The produced substance is a liquid with purity between 25 to 40%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use

The frequency of events associated with this use is expected to be sporadic.

Environmental factors influenced by risk management

Waste stream treatment may be employed to reduce environmental exposure. Emissions to air may be as much as 34.2 kg/d but are generally much less.

Other operational conditions affecting environmental exposure

The use of lead acid batteries containing sulphuric acid takes place in outdoor facilities.

Technical conditions and measures at process level (source) to prevent release

No additional technical measures in place to prevent release.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Waste stream treatment may be employed to reduce environmental exposure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste stream treatment may be employed to reduce environmental exposure.

Conditions and measures related to external treatment of waste for disposal

There is no further generation of solid waste

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

11.2 Controlling worker exposure for ES 11

ES 11: CES 2: consumer exposure arising due to hand-mixing with intimate contact and only PPE available (PROC 19).

During the use of lead acid batteries containing sulphuric acid, controlled systems are in place to reduce the potential for consumer exposure in all cases.

Loading and unloading of vessels of sulphuric acid for use in maintenance of batteries is usually performed in the open air. Consumers are advised to wear protective clothing, however, the worst case assumption is that no localised controls are used in the process.

Product characteristics

The produced substance is a liquid with purity between 25 to 40%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 2,500 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, these activities are expected to be short duration tasks and 8 hours per day is considered to be a worst case assumption.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

The use of lead acid batteries containing sulphuric acid is generally carried out by the public in facilities which are not expected to have specific exposure controls and waste treatment measures in place. Individuals involved in the loading and unloading of vessels of sulphuric acid for use in the maintenance of batteries is usually performed in the open air. Consumers are advised to wear protective clothing, however, the worst case assumption is that no localised controls are used in the process.

Technical conditions and measures at process level (source) to prevent release

No specific localized control measures are in place.

Technical conditions to control dispersion from source towards worker

No specific localized control measures are expected to be in place.

Organizational measures to prevent/limit release

Consumers are advised to wear protective clothing, however, the worst case assumption is that no localised controls are used in the process.

Conditions and measures related to personal protection, hygiene and health.

It is advisable that consumers wear suitable protective clothing but no localized controls are expected to be in place.

11.3 Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|--|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 8.99 x 10 ⁻⁵ | |
| Marine water (in mg/L) | 5.83 x 10 ⁻⁵ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 7.23 x 10 ⁻⁵ | |
| Marine sediment (in mg/kg) | 4.69 x 10 ⁻⁵ | |
| Agricultural soil (averaged over 30 days (in mg/kg) | 2.96 x 10 ⁻⁴ | |
| Groundwater (in mg/L) | 1.35 x 10 ⁻³ | |
| Annual average PEC in air, total (mg/m ³) | 9.52 x 10 ⁻³ | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|------------------------------|-------------------------|--------------|----------|---|
| ERC 9B Tier 1 Freshwater | 5.64 x 10 ⁻⁵ | 0.0025 | 0.22 | Safe use in tier 1 for all compartments |
| ERC 9BTier 1 Sediment | 1.84 x 10 ⁻⁵ | 0.002 (EPM) | 0.092 | |
| ERC 9BTier 1 Marine | 5.64 x 10 ⁻⁵ | 0.00025 | 0.22 | |
| ERC 9BTier 1 Marine sediment | 4.69 x 10 ⁻⁵ | 0.002 (EPM) | 0.0023 | |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 11, the 90th percentile (e.g.

worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 11. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 11 do not pose an unacceptable health risk to workers.

Information for worker contributing scenario 2:

| | PROC | Parameters/ assumptions |
|-----------------------------------|---------|---|
| Exposure duration | PROC 19 | 240 mins exposure / day; 240 mins |
| | | non-exposure/day |
| Product type | PROC 19 | Liquid (low viscosity – like water) |
| Process temperature | PROC 19 | Room temperature (15-25oC) |
| Vapour pressure | PROC 19 | 6 Pa – Substance is considered to be |
| | | low volatile, exposure to mists is |
| | | estimated |
| Liquid weight fraction | PROC 19 | 0.25 |
| Primary emission source proximity | PROC 19 | Primary emission source located in |
| | | the breathing zone of the workers (i.e. |
| | | Within 1 metre) |
| Activity class | PROC 19 | Handling of contaminated objects |
| Localised controls | PROC 19 | None |
| Fugative emission source | PROC 19 | Not fully enclosed – effective |
| - | | housekeeping practices in place |
| Dispersion | PROC 19 | Indoors, any sized room, only good |
| - | | natural ventilation |

List of inputs used in the ART assessment

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Exposure (mg/m3) | Short-term Concentrations | Estimated Exposure (mg/m3) | Long-term Concentration |
|---|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Hand-mixing with intimate contact: only PPE available | 19 | Liquid | 0.00058 | 0.0023 | 0.00079 | 0.002 |

List of derived RCRs

| ſ | Acute-local effects | CES 2 | PROC 19 | 2.3 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻² |
|---|------------------------------|-------|---------|------------------------|--|------|------------------------|
| | Long-term – local effects | CES 2 | PROC 19 | 2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 4 x 10 ⁻² |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

| 11.4 | Guidance to DU to evaluate whether he works inside the boundaries set by the ES |
|------|---|
| | • |

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 34.2 kg per day
- Waste stream treatment may be employed to reduce environmental exposure.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- Consumers are advised to wear appropriate protective clothing in the use and handling of sulphuric acid.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 11.5 | Additional good practice advice beyond the REACH CSA. |
|--|--|
| Alwa surfa Worfacid | not eat, drink or smoke when working with sulphuric acid. ays wash hands and exposed skin thoroughly after using sulphuric acid or any aces/machinery that may have come into contact with sulphuric acid. kers should be suitably trained in all safety procedures and in the safe handling of sulphuric to prevent risk of exposure. PPE should be properly maintained and stored in an appropriate way so as not to damage its |

All PPE should be properly maintained and stored in an appropriate way so as not to damage i integrity. Workers should be correctly trained in its use.

- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

12 Exposure Scenario 12: Use of sulphuric acid as a laboratory chemical

Use of sulphuric acid as a laboratory chemical

Processes Covered:

Environmental Releases

ERC08a: Wide dispersive indoor use of processing aids in open systems ERC08b: Wide dispersive indoor use of reactive substances in open systems

Worker Processes

PROC15: Use as laboratory reagent

Produce Category PC21: Laboratory chemicals

Sulphuric acid may be used as laboratory agent in buffers, in protein reagents and as acidification reagents. Uses would generally be on a smaller scale and would not be intensive. Sulphuric acid may be used in laboratories in a diluted form as the uses of acid in laboratory science are so diverse.

Because of the processes involved in the use of sulphuric acid as a laboratory agent, (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid as a laboratory reagent. (ERC 08a and ERC 08b).

Contributing Worker Scenarios: CES 2: worker exposure arising due to use as a laboratory reagent (PROC 15).

12.1 Controlling environmental exposure for ES 12

ES12: Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid as a laboratory reagent.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid as a laboratory reagent. Environmental emissions are limited by waste capture strategies including the use of flow hoods with gaseous removal and dedicated effluent capture treatment facilities are generally

employed. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Use of sulphuric acid as a laboratory reagent is generally continuous with constant production and use. Facilities generally use up to 5,000 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 5,000 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

Dedicated effluent capture treatment facilities are used. Emissions to air may be as much as 1,370 kg/d but are generally much less. Exhaust gases may be treated by the use of flow hoods with gaseous removal capabilities.

Other operational conditions affecting environmental exposure

The use of sulphuric acid as a laboratory reagent takes place indoors. Any gas displaced from containers is conducted via pipeline to be processed i.e. removed and scrubbed and /or filtered.

Technical conditions and measures at process level (source) to prevent release

Laboratory use and handling of sulphuric acid occurs indoors and involves special equipment with little or no potential for exposure.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Waste stream treatment may be used to reduce environmental exposure however for this wide dispersive use particular risk management measures are not needed to demonstrate environmental safe use for laboratories. All gas emissions are scrubbed and filtered through the use of flow hoods to capture any gaseous emissions.

Organizational measures to prevent/limit releases from site

Workers using sulphuric acid in a laboratory are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste waters are generally treated on site.

Conditions and measures related to external treatment of waste for disposal

Waste stream treatment and gaseous capture through the use of flow hoods may be used to reduce environmental exposure however for this wide dispersive use particular risk management measures are not needed to demonstrate environmental safe use for laboratories. There is no further generation of solid waste

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Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

12.2

Controlling worker exposure for ES 12

ES 12: CES 2: worker exposure arising due to use as a laboratory reagent (PROC 15).

During the use of sulphuric acid as a laboratory reagent, controlled systems are in place to reduce the potential for worker exposure in all cases.

Workers involved in the handling and transfer of materials are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks. LEV is generally used to ensure adequate control of gaseous emissions.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 5,000 tonnes per year which is considered to be a worst case assumption

for a single site in Europe, operating 365 days per year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, the activities associated with the use of sulphuric acid as a laboratory reagent are expected to be short duration tasks and 8 hours per day is a worst case assumption.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Sulphuric acid is used as a laboratory reagent by trained personnel. LEV and the use of flow hoods to capture gaseous emissions reduce the potential for exposure. Controlled systems are also employed with little or no potential for exposure. Workers involved in the handling and transfer of materials are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks.

Technical conditions and measures at process level (source) to prevent release

LEV and the use of flow hoods to capture gaseous emissions reduce the potential for exposure.

Technical conditions to control dispersion from source towards worker

Any gas displaced during the use of sulphuric acid as a laboratory reagent is captured in flow hoods to be scrubbed and /or filtered. During the use of sulphuric acid as a laboratory reagent, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring. Organizational measures to prevent/limit release

Workers involved in the handling and transfer of materials are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks. Conditions and measures related to personal protection, hygiene and health.

Anti-acid gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

12.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control

environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|--|-------------------------|-----------------------------------|
| ERC 8a Freshwater (in mg/L) | 1.34 x 10 ⁻⁴ | Wide dispersive dilution. |
| ERC 8a Marine water (in mg/L) | 6.04 x 10 ⁻⁶ | |
| ERC 8a Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| ERC 8a Freshwater sediment (in mg/kg) | 1.08 x 10 ⁻⁴ | |
| ERC 8a Marine sediment (in mg/kg) | 6.04 x 10 ⁻⁶ | |
| ERC 8a Agricultural soil (averaged over 30 days (in mg/kg) | 6.42 x 10 ⁻³ | |
| ERC 8a Groundwater (in mg/L) | 0.0213 | |
| ERC 8a Annual average PEC in air, total (mg/m ³) | 0.381 | |
| ERC 8b Freshwater (in mg/L) | 2.12 x 10 ⁻⁶ | Wide dispersive dilution. |
| ERC 8b Marine water (in mg/L) | 5.54 x 10 ⁻⁸ | |
| ERC 8b Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| ERC 8b Freshwater sediment (in mg/kg) | 1.7 x 10 ⁻⁶ | |
| ERC 8b Marine sediment (in mg/kg) | 5.54 x 10 ⁻⁸ | |
| ERC 8b Agricultural soil (averaged over 30 days (in mg/kg) | 1.1 x 10 ⁻⁴ | |
| ERC 8b Groundwater (in mg/L) | 1.49 x 10 ⁻⁴ | |
| ERC 8b Annual average PEC in air, total (mg/m ³) | 3.81 x 10 ⁻⁴ | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|----------------------------------|-------------------------|--------------|------------------------|---|
| ERC 8A Tier 1 Freshwater | 1.34 x 10 ⁻⁴ | 0.0025 | 0.0536 | Safe use in tier 1 for all compartments |
| ERC 8A Tier 1 Sediment | 2.67 x 10 ⁻⁵ | 0.002 (EPM) | 0.013 | |
| ERC 8A Tier 1 Marine sediment | 6.04 x 10 ⁻⁶ | 0.002 (EPM) | 0.003 | |
| ERC 8A Tier 1 Marine | 1.08 x 10 ⁻⁴ | 0.00025 | 0.43 | |
| ERC 8B Tier 1 Freshwater | 2.21 x 10 ⁻⁶ | 0.0025 | 8.8 x 10 ⁻⁴ | Safe use in tier 1 for all compartments |
| ERC 8BTier 1 Sediment | 1.7 x 10 ⁻⁶ | 0.002 (EPM) | 8.5 x 10 ⁻⁴ | |
| ERC 8BTier 1 Marine sediment | 5.54 x 10 ⁻⁸ | 0.002 (EPM) | 2.7 x 10 ⁻⁵ | |

| 2.1×10^{-4} |
|----------------------|
|----------------------|

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 12, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 12. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 12 do not pose an unacceptable health risk to workers.

Information for worker contributing scenario 2:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|---------|---|
| Exposure duration | PROC 15 | 240 mins exposure / day; 240 mins |
| - | | non-exposure/day |
| Product type | PROC 15 | Liquid (medium viscosity – like oil) |
| Process temperature | PROC 15 | Room temperature (15-25oC) |
| Vapour pressure | PROC 15 | Substance is considered to be low |
| | | volatile, exposure to mists is |
| | | estimated |
| Liquid weight fraction | PROC 15 | 0.98 |
| Primary emission source proximity | PROC 15 | Primary emission source located in |
| | | the breathing zone of the workers (i.e. |
| | | Within 1 metre) |
| Activity class | PROC 15 | Transfer of liquids |
| Localised controls | PROC 15 | LEV |
| Fugative emission source | PROC 15 | Not fully enclosed – effective |
| - | | housekeeping practices in place |
| Dispersion | PROC 15 | Indoors, any sized room, only good |
| - | | natural ventilation |

List of derived exposure concentrations

| Description of activity | PROC | J | Estimated | Short-term | | Long-term |
|-------------------------|------|----------------------|---------------------|----------------|------------------|---------------|
| | | state of material | Exposure (mg/m3) | Concentrations | Exposure (mg/m3) | Concentration |
| | | | | | | |

| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
|--|----|--------|---|---|---|---|
| Handling sulphuric acid in a aboratory | 15 | Liquid | 6.8 x 10-5 | 2.7 x 10-4 | 9.3 x 10-5 | 2.3 x 10-4 |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 12- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|--|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 15 | 2.7 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 2.7 x 10 ⁻³ |
| Long-term – local effects | CES 2 | PROC 15 | 2.3 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 4.6 x 10 ⁻³ |

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from

the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

12.4 Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 1,370 kg per day
- Waste stream treatment may be used to reduce environmental exposure.
- Gas displaced following use of sulphuric acid as a laboratory reagent is captured in flow hoods and is scrubbed and /or filtered.
- Sufficient LEV and vapour recovery systems are in place to reduce exposure.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- LEV and the use of flow hoods to capture gaseous emissions reduce the potential for exposure.
- Workers should wear protective anti-acid gloves, goggles, overalls and boots at all times in the production and transfer area.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

12.5 Additional good practice advice beyond the REACH CSA.

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

| 13 | Exposure Scenario 13: Use of sulphuric acid in industrial cleaning |
|----|--|
| | |

Use of sulphuric acid in industrial cleaning

Processes Covered:

Environmental Releases

ERC08a: Wide dispersive indoor use of processing aids in open systems ERC08b: Wide dispersive indoor use of reactive substances in open systems

Worker Processes

PROC02: Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance)

PROC05: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant con-tact)

PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC09: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

PROC10: Roller application or brushing

PROC13: Treatment of articles by dipping and pouring

Produce Category

PC35: Washing and cleaning products (including solvent based products)

Sulphuric acid as a component or feedstock in heavy duty industrial cleaners. This use would not be very regular and would generally be used in cases of heavy industrial contamination.

Because of the processes involved in the use of sulphuric acid as a laboratory agent, (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in industrial cleaning. (ERC 08a and ERC 08b).

Contributing Worker Scenarios: CES 2: worker exposure due to day to day use in closed continuous processes with occasional exposure (such as sampling) (PROC 2), CES 3: worker exposure due to mixing or blending in batch processes for formulation of preparations and articles in an industrial setting (PROC 5), CES 4: worker exposure due to transfer of substance to and from vessels and containers at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 5: worker exposure due to transfer of formulations or preparations to small containers (PROC 9), CES 6: worker exposure due to roller and brushing application (PROC 10) and CES 7: worker exposure due to treatment of articles by dipping and pouring (PROC 13).

13.1 Controlling environmental exposure for ES 13

ES13 Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid industrial cleaning.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in industrial cleaning. Environmental emissions are limited by emission to the STP. Waste stream treatment may also be employed to reduce environmental exposure however for this wide dispersive use particular risk management measures are not needed to demonstrate environmental safe use.

In addition to this, as the amounts used are low and pre-diluted, dilution in the waste stream is expected to be significant, thus reducing the exposure to the environment.

Use of sulphuric acid as a laboratory reagent is generally continuous with constant production and use. Facilities generally use up to 5,000 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Product characteristics

The produced substance is a liquid with purity of 10%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities generally use up to 5,000 tonnes per year which is considered to be a worst case assumption for a single site in Europe, operating 365 days per year.

Frequency and duration of use

Use is expected to be infrequent in varying amounts.

Environmental factors influenced by risk management

Environmental emissions are directed to the STP. Emissions to air may be as much as 1,370 kg/d but are generally much less. Exhaust gases are removed by LEV.

Other operational conditions affecting environmental exposure

The use of sulphuric acid in industrial cleaning takes place indoors in controlled environments. Any gas displaced from containers is removed by LEV.

Technical conditions and measures at process level (source) to prevent release

Sulphuric acid used in industrial cleaning is used by trained personnel under controlled conditions. LEV is in place to capture any gaseous emissions. All emissions are directed to the STP for treatment before emission to the environment.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Environmental emissions are limited by emission to the STP. Waste stream treatment may also be employed to reduce environmental exposure. All gas emissions are captured by LEV to prevent any gaseous emissions.

Organizational measures to prevent/limit releases from site

Workers using sulphuric acid in industrial cleaning are fully trained in order to prevent accidental release.

Conditions and measures related to municipal STP

Waste emissions are treated in the onsite STP.

Conditions and measures related to external treatment of waste for disposal

Environmental emissions are limited by emission to the STP. Waste stream treatment may also be employed to reduce environmental exposure. There is no further generation of solid waste

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

13.2

Controlling worker exposure for ES 13

ES 13: CES 2: worker exposure due to day to day use in closed continuous processes with occasional exposure (such as sampling) (PROC 2), CES 3: worker exposure due to mixing or blending in batch processes for formulation of preparations and articles in an industrial setting (PROC 5), CES 4: worker exposure due to transfer of substance to and from vessels and containers at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 5: worker exposure due to transfer of formulations or preparations to small containers (PROC 9), CES 6: worker exposure due to roller and brushing application (PROC 10) and CES 7: worker exposure due to treatment of articles by dipping and pouring (PROC 13).

During the use of sulphuric acid in industrial cleaning, controlled systems are in place to reduce the potential for worker exposure in all cases.

Loading and unloading of vessels of sulphuric acid for use in maintenance of batteries is usually performed in the open air. Workers wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage. LEV is generally used to ensure adequate control of gaseous emissions.

Product characteristics

The produced substance is a liquid with purity of 10%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive. Amounts used

Facilities generally use up to 5,000 tonnes per year which is considered to be a worst case assumption

for a single site in Europe, operating 365 days per year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, the activities associated with the use of sulphuric acid in industrial cleaning are expected to be short duration tasks and 8 hours per day is a worst case assumption.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Industrial cleaning using sulphuric acid is conducted by trained personnel. LEV is in place to capture gaseous emissions, reducing the potential for exposure. Workers involved in the loading/unloading of sulphuric acid or the handling of sulphuric acid wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overall). Workers are also trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks.

Technical conditions and measures at process level (source) to prevent release

LEV used to capture gaseous emissions reduces the potential for exposure.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is removed by LEV. During the use of sulphuric acid as a laboratory reagent, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring.

Organizational measures to prevent/limit release

Workers involved in the handling and transfer of materials are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks. Conditions and measures related to personal protection, hygiene and health.

Anti-acid gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

13.3 Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|-------------------------------|-------------------------|---------------------------|
| ERC 8a Freshwater (in mg/L) | 1.34 x 10 ⁻⁴ | Wide dispersive dilution. |
| | | |
| ERC 8a Marine water (in mg/L) | 6.04 x 10 ⁻⁶ | |

| ERC 8a Intermittent releases to water (in | NA | Intermittent release not relevant |
|--|-------------------------|-----------------------------------|
| mg/L) | | |
| ERC 8a Freshwater sediment (in mg/kg) | 1.08 x 10 ⁻⁴ | |
| ERC 8a Marine sediment (in mg/kg) | 6.04 x 10 ⁻⁶ | |
| ERC 8a Agricultural soil (averaged over 30 days (in mg/kg) | 6.42 x 10 ⁻³ | |
| ERC 8a Groundwater (in mg/L) | 0.0213 | |
| ERC 8a Annual average PEC in air, total (mg/m^3) | 0.381 | |
| ERC 8b Freshwater (in mg/L) | 2.12 x 10 ⁻⁶ | Wide dispersive dilution. |
| ERC 8b Marine water (in mg/L) | 5.54 x 10 ⁻⁸ | |
| ERC 8b Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| ERC 8b Freshwater sediment (in mg/kg) | 1.7 x 10 ⁻⁶ | |
| ERC 8b Marine sediment (in mg/kg) | 5.54 x 10 ⁻⁸ | |
| ERC 8b Agricultural soil (averaged over 30 days (in mg/kg) | 1.1 x 10 ⁻⁴ | |
| ERC 8b Groundwater (in mg/L) | 1.49 x 10 ⁻⁴ | |
| ERC 8b Annual average PEC in air, total (mg/m ³) | 3.81 x 10 ⁻⁴ | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|----------------------------------|-------------------------|--------------|------------------------|---|
| ERC 8A Tier 1 Freshwater | 1.34 x 10 ⁻⁴ | 0.0025 | 0.0536 | Safe use in tier 1 for all compartments |
| ERC 8A Tier 1 Sediment | 2.67 x 10 ⁻⁵ | 0.002 (EPM) | 0.013 | |
| ERC 8A Tier 1 Marine sediment | 6.04 x 10 ⁻⁶ | 0.002 (EPM) | 0.003 | |
| ERC 8A Tier 1 Marine | 1.08 x 10 ⁻⁴ | 0.00025 | 0.43 | |
| ERC 8B Tier 1 Freshwater | 2.21 x 10 ⁻⁶ | 0.0025 | 8.8 x 10 ⁻⁴ | Safe use in tier 1 for all compartments |
| ERC 8BTier 1 Sediment | 1.7 x 10 ⁻⁶ | 0.002 (EPM) | 8.5 x 10 ⁻⁴ | |
| ERC 8BTier 1 Marine sediment | 5.54 x 10 ⁻⁸ | 0.002 (EPM) | 2.7 x 10 ⁻⁵ | |
| ERC 8BTier 1 Marine | 5.54 x 10 ⁻⁸ | 0.00025 | 2.1 x 10 ⁻⁴ | |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 13, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value for long-term local respiratory effects respectively for any of the processes associated with ES 13. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 13 do not pose an unacceptable health risk to workers.

Information for worker contributing scenario 2, 3, 4, 5, 6 and 7:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|--------------------|--|
| Exposure duration | All | 480 mins |
| Product type | All | Liquid (low viscosity – like water) |
| Process temperature | All | Room temperature (15-25°C) |
| Vapour pressure | All | Substance is considered to be low volatile, exposure to mists is estimated |
| Liquid weight fraction | All | 0.1 |
| Primary emission source proximity | All | Primary emission source located in the breathing zone of the workers (i.e. Within 1 metre) |
| Activity class | PROC 2,8a,8b,9 | Transfer of liquid products |
| | PROC 5,13 | Activities with open liquid surface or reservoirs |
| | PROC 10 | Spreading of liquid products |
| Containment | PROC 2,8a,9 | Handling reduces contact between product and adjacent air |
| | PROC 5,8b,10,13 | n/a |
| Localised controls | PROC 2,5 | LEV |
| | PROC,8a,8b,9,10,13 | none |
| Fugative emission source | All | Not fully enclosed – effective housekeeping practices in place |
| Dispersion | All | Indoors, any sized room, only good natural ventilation |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Short-term Exposure Concentrations (mg/m ³) | | Estimated Long-term Exposure Concentration (mg/m ³) | |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed, continuous process with occasional controlled exposure (including sampling and maintenance) | 2 | Liquid | 1.40E-04 | 0.00055 | 1.90E-04 | 4.80E-04 |
| Mixing or blending in batch process for formulation of | 5 | Liquid | 0.015 | 0.061 | 0.021 | 0.053 |

| preparations or articles | | | | | | |
|--------------------------------|-----|--------|----------|--------|----------|---------|
| (multistage and/or significant | | | | | | |
| contact) | | | | | | |
| Transfer of 10% sulphuric | 8a | Liquid | 0.0014 | 0.0055 | 0.0019 | 0.0048 |
| acid cleaning solution | | | | | | |
| to/from large | | | | | | |
| vessels/containers at | | | | | | |
| dedicated facilities | | | | | | |
| Transfer of 10% sulphuric | 8b | Liquid | 0.0014 | 0.0055 | 0.0019 | 0.0048 |
| acid cleaning solution | | | | | | |
| to/from large | | | | | | |
| vessels/containers at non- | | | | | | |
| dedicated facilities | | | | | | |
| Filling small containers with | 9 | Liquid | 0.0014 | 0.0055 | 0.0019 | 0.0048 |
| 10% sulphuric acid cleaning | | | | | | |
| solution | | | | | | |
| Applying 10% sulphuric acid | 10 | Liquid | 0.15 | 0.61 | 0.21 | 0.53 |
| cleaning solutions using | | | | | | |
| brush or roller. | 1.0 | ~ | | 0.0074 | | 0.00.50 |
| Cleaning articles by | 13 | Liquid | 1.50E-03 | 0.0061 | 2.10E-03 | 0.0053 |
| dipping/immersing in 10% | | | | | | |
| sulphuric acid solution | | | | | | |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 13- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|--|---|-----------------|---|
| Acute-local effects | CES 2 | PROC 2 | 5.5 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 5.5 x 10 ⁻³ |
| | CES 3 | PROC 5 | 6.1 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 6.1 x 10 ⁻¹ |
| | CES 4 | PROC 8a | 5.5 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 5.5 x 10 ⁻² |
| | | PROC 8b | 5.5 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 5.5 x 10 ⁻² |
| | CES 5 | PROC 9 | 5.5 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 5.5 x 10 ⁻² |
| | CES 6 | PROC 10 | 6.1 x 10 ⁻¹ (3 x 10 ⁻²)* | Respiratory irritation and corrositivity | 0.1 | 6.1 x 10 ⁰ (3 x 10 ⁻¹)* |
| | CES 7 | PROC 13 | 6.1 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 6.1 x 10 ⁻² |
| Long-term – local effects | CES 2 | PROC 2 | 4.8 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻³ |
| | CES 3 | PROC 5 | 5.3 x 10 ⁻² (2.7 x 10 ⁻³)* | Respiratory irritation and corrositivity | 0.05 | 1.1 x 10 ⁰ (5.3 x 10 ⁻²)* |

| CES 4 | PROC 8a | 4.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻² |
|-------|---------|--|--|------|--|
| | PROC 8b | 4.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻² |
| CES 5 | PROC 9 | 4.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻² |
| CES 6 | PROC 10 | 5.3 x 10 ⁻¹ (2.7 x 10 ⁻²)* | Respiratory irritation and corrositivity | 0.05 | $ \begin{array}{c} 1.1 \times 10^{1} \\ (0.54)^{*} \end{array} $ |
| CES 7 | PROC 13 | 5.3 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 1.1 x 10 ⁻¹ |

*Assumes Respiratory Protective Equipment (95% reduction) is worn

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from

any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

13.4

Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 1,370 kg per day
- Environmental emissions are limited by emission to the STP.
- Waste stream treatment may be used to reduce environmental exposure.
- Gas displaced following use of sulphuric acid in industrial cleaning is processes with the use of LEV.
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- LEV is in place to capture gaseous emissions and reduce the potential for exposure.
- Workers should wear protective anti-acid gloves, goggles, overalls and boots at all times in the production and transfer area.
- Workers should be suitably trained in the correct use of all machinery and PPE used in industrial cleaning.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

13.5 Additional good practice advice beyond the REACH CSA.

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly

| 14 | Exposure Scenario 14: Use of sulphuric acid in the mixing, preparation and repackaging |
|----|--|
| | of sulphuric acid. |

Use of sulphuric acid in the mixing, preparation and repackaging of sulphuric acid.

Processes Covered:

Environmental Releases

ERC02: Formulation of preparations

Worker Processes

PROC01: Use in closed process, no likelihood of exposure

PROC03: Use in closed batch process (synthesis or formulation)

PROC05: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact)

PROC08a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

PROC08b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC09: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

Sulphuric acid may be used during mixing, repackaging, preparation and in the production of oleum. Oleum is produced using sulphur trioxide which is dissolved in concentrated sulphuric acid. Sulphuric acid is used in this manner is generally recycled by dilution of the produced oleum.

Because of the processes involved in the use of sulphuric acid, (and the nature of sulphuric acid and the produced gases), specially trained workers and systems are employed.

Contributing Environmental Scenario: CES1 Environmental exposure arising due to the use of sulphuric acid in the mixing, preparation and repackaging of sulphuric acid. (ERC 02).

Contributing Worker Scenarios: CES 2: worker exposure due to day to day use in closed processes, no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to day to day use in closed batch process (PROC 3), CES 4: worker exposure due to mixing or blending in batch processes for formulation of preparations and articles in an industrial setting (PROC 5), CES 5: worker exposure due to transfer of substance to and from vessels and containers at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 6: worker exposure due to transfer of formulations or preparations to small containers (PROC 9).

14.1 Controlling environmental exposure for ES 14

ES14 Contributing exposure scenario (CES) 1 Environmental exposure arising due to use of sulphuric acid in the mixing, preparation and repackaging of sulphuric acid.

Section 2.1 describes the environmental releases that may occur during the use of sulphuric acid in the mixing, preparation and repackaging of sulphuric acid. These releases may potentially occur due to emission to wastewater or through emission to the atmosphere. Environmental emissions are limited by designated waste treatment process designed to limit environmental exposure to all relevant compartments. Waste gas emissions are scrubbed and may also then be diverted to the wastewater stream. This significantly lessens the possible emission by atmospheric deposition to soil or surface waters.

Liquid wastes are treated (neutralization to neutral pH) prior to emission to remove any sulphuric acid in the waste water and sludge from the waste water treatment plant is sent for incineration or landfill and is not used for agricultural spreading. This precludes any contamination of soil by sludge spreading. Waste water treatment is usually carried out by neutralisation followed by flocculation or decantation.

Use of sulphuric acid in mixing, preparation and repackaging is generally continuous with constant production and use. Facilities may generally produce between 100 and 500 tonnes per day in a large facility, with up to 300,000 tonnes produced per year at the largest European manufacturing plant in a working year of 365 days. This value has been considered as a worst case assumption for this environmental exposure scenario.

Product characteristics

The produced substance is a liquid with purity of greater than 90 %. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities may generally produce between 100 and 500 tonnes per day in a large facility, with up to 300,000 tonnes produced per year at the largest European manufacturing plant operating 365 days a year. This value has been considered as a worst case assumption for this environmental exposure scenario.

Frequency and duration of use

Continuous production and release.

Environmental factors influenced by risk management

On site WWTP with the capacity for complete neutralization. Emissions to air may be as much as 205

kg/d but are generally much less.

Other operational conditions affecting environmental exposure

Use of sulphuric acid in mixing, preparation and repackaging takes place in a highly specialized indoor facility with emissions to water being fully neutralized before release. Reactors and transfer pipelines are closed systems. Waste gas emissions are scrubbed and may also be diverted to the wastewater stream.

Technical conditions and measures at process level (source) to prevent release

As mentioned above reactors and pipelines are fully sealed. Both production and sampling are carried out in dedicated facilities. Transfer operations are carried out under controlled conditions in sealed systems to reduce potential losses.

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

Sulphuric acid is used in mixing, preparation and repackaging on a large scale, generally on major chemical sites, which will have dedicated effluent treatment facilities, involving both chemical and biological treatment, coping with many chemical substances. As such any emission to wastewater will be almost instantly hydrolysed before even reaching the STP.

Neutralisation procedures are in place to ensure that the pH of any downstream biological treatment or final receiving waters is not affected. All waste waters should be treated in this manner. Measured pH values can be used to confirm the efficacy of the neutralization procedure.

Organizational measures to prevent/limit releases from site

Workers are fully trained in order to prevent accidental release. The gaseous outflow is continually analysed for waste gases associated with sulphuric acid use.

Conditions and measures related to municipal STP

Emissions to the municipal STP should not be made. All waste water should be treated in the on-site waste water treatment plant. Precipitated sludge should be sent for specialized waste treatment and should not be spread to soil.

Conditions and measures related to external treatment of waste for disposal

Sludge from the on-site WWTP would normally be sent to specialized landfill or for incineration at a dedicated waste facility. Waste from any scrubbers should be directed to waste water. There is no further generation of solid waste.

Conditions and measures related to external recovery of waste

There is no envisaged external recovery of waste.

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14.2

Controlling worker exposure for ES 14

ES 14: CES 2: worker exposure due to day to day use in closed processes, no likelihood of exposure (PROC 1), CES 3: worker exposure arising due to day to day use in closed batch process (PROC 3), CES 4: worker exposure due to mixing or blending in batch processes for formulation of preparations and articles in an industrial setting (PROC 5), CES 5: worker exposure due to transfer of substance to and from vessels and containers at non-dedicated and dedicated facilities (PROC 8a and PROC 8b), CES 6: worker exposure due to transfer of formulations or preparations to small containers (PROC 9).

During the use of sulphuric acid mixing, preparation and repackaging, controlled systems are in place to reduce the potential for worker exposure in all cases.

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Loading and unloading of tankers with sulphuric acid or oleum is usually performed in the open air.

Workers wear protective clothing (face/eye protection, respiratory protection, helmet, anti-acid gloves boots and protective overall). A safety shower is required nearby in case of accidental spillage. Gas displacement lines are also used if filling of road tankers takes place under cover.

Product characteristics

The produced substance is a liquid with purity greater than 90%. The substance is colourless, odourless inorganic liquid which is miscible with water. Sulphuric acid is not flammable and is non-explosive.

Amounts used

Facilities may generally produce between 100 and 500 tonnes per day in a large facility, with up to 300,000 tonnes produced per year at the largest European manufacturing plant operating 365 days a year.

Frequency and duration of use exposure

Workers perform standard shifts of 8 hours per day and have standard working years of 220 days per year. However, the activities associated with this exposure scenario are not expected to take 8 hours to complete and so, are considered to be a worst case assumption.

Human factors not influenced by risk management

Respiration volumes under conditions of use $10m^3/d$ (default value for a worker breathing for an 8h work day in RIP 3.2).

Other given operational conditions affecting worker exposure

Mixing, preparing and repackaging sulphuric acid is conducted by trained personnel. LEV is in place to capture gaseous emissions, reducing the potential for exposure. Workers involved in the

loading/unloading of sulphuric acid or the handling of sulphuric acid wear protective clothing (face/eye protection, helmet, anti-acid gloves boots and protective overalls). Workers are also trained in the correct and appropriate handling procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks.

Technical conditions and measures at process level (source) to prevent release

LEV used to capture gaseous emissions reduces the potential for exposure.

Technical conditions to control dispersion from source towards worker

Any gas displaced from containers is removed by LEV. During the use of sulphuric acid as a laboratory reagent, special equipment and controlled systems with little or no potential for exposure are used to prevent losses occurring. Workers are generally separated from the machinery and installations housing the machinery to minimize the potential for exposure.

Organizational measures to prevent/limit release

Workers involved in the handling and transfer of materials are trained in the procedures and protective equipment is intended to cope with the worst case scenario, in order to minimise exposure and risks. Conditions and measures related to personal protection, hygiene and health.

Anti-acid gloves, goggles, chemical resistant overalls and work boots are worn by all operators in the facility to prevent dermal exposure.

14.3

Exposure estimation and reference to its source

Environmental Exposure

For the tier 1 risk characterisation PECs derived using the ERC defaults are not assessed below as the PECs are considered unrealistically high and would lead to a failing risk assessment in any case. For the tier 2 risk characterisation the PECs calculated by the EUSES environmental model with refined inputs taking into account the emission RMMs as discussed in section 2.1 above are used to control

environmental releases are used for the assessment.

Information for contributing exposure scenario 1:

List of exposure concentrations

| Compartment | PEC | Justification |
|---|-------------------------|-----------------------------------|
| Freshwater (in mg/L) | 4.43 x 10 ⁻⁵ | Wide dispersive dilution. |
| Marine water (in mg/L) | 6.42 x 10 ⁻⁶ | |
| Intermittent releases to water (in mg/L) | NA | Intermittent release not relevant |
| Freshwater sediment (in mg/kg) | 3.56 x 10 ⁻⁵ | |
| Marine sediment (in mg/kg) | 5.16 x 10 ⁻⁶ | |
| Agricultural soil (averaged over 30 days | 9.42 x 10 ⁻⁴ | |
| (in mg/kg) | | |
| Groundwater (in mg/L) | 0.007 | |
| Annual average PEC in air, total (mg/m ³) | 0.0571 | |

The following RCRs were derived taking into account derived PNEC values

| Compartments | PEC mg/L | PNEC mg/L | PEC/PNEC | Comments |
|---------------------------|-------------------------|--------------|----------|---------------------------------------|
| Tier 2 Freshwater | 4.43 x 10 ⁻⁵ | 0.0025 | 0.01 | Safe use demonstrated in tier 2 |
| Tier 2 Sediment | 3.56 x 10 ⁻⁵ | 0.002 (EPM) | 0.0178 | Safe use demonstrated in tier 2 |
| Tier 2 Marine sediment | 5.16 x 10 ⁻⁶ | 0.002 (EPM | 0.0025 | Safe use demonstrated in tier 2 |
| Tier 2 Marine | 6.42 x 10 ⁻⁶ | 0.00025 | 0.0256 | Safe use demonstrated in tier 2 |

* EPM = equilibrium partitioning method

Worker exposure

The Advanced REACH tool (ART) was used to estimate worker exposure as it was considered that the ECETOC model cannot estimate in a satisfactory manner the effects of the stringent containment and segregation practices which are in place to deal with sulphuric acid production and to limit exposure.

In the characterisation of the human health risks posed by acute/short term and long-term inhalation exposures to sulphuric acid (or formed sulphuric acid) associated with ES 14, the 90th percentile (e.g. worst case) inhalation exposure concentrations derived using the ART model for relevant PROC codes were compared with the DNEL value for acute local respiratory effects and the DNEL value for long-term local respiratory effects respectively. The results of the risk characterisation are shown in the table below.

The predicted acute/short-term and long-term inhalation exposure concentrations derived using the ART model were not found to exceed the DNEL value for acute local respiratory effects or the DNEL value

for long-term local respiratory effects respectively for any of the processes associated with ES 14. On the basis of the assumptions made in the exposure assessment and this risk characterisation, it can be concluded that inhalation exposures to sulphuric acid that may potentially arise during processes associated with ES 14 do not pose an unacceptable health risk to workers.

Information for worker contributing scenario 2, 3, 4, 5 and 6:

List of inputs used in the ART assessment

| | PROC | Parameters/ assumptions |
|-----------------------------------|------------------|--|
| Exposure duration | All | 480 mins |
| Product type | All | Liquid (medium viscosity – like oil) |
| Process temperature | PROC 1,3 | Hot processes (50-150oC) |
| | PROC 5,8a,8b, 9 | Room temperature (15-25oC) |
| Vapour pressure | All | Substance is considered to be low volatile, exposure to mists is estimated |
| Liquid weight fraction | All | 0.98 |
| Primary emission source proximity | PROC 1, | Primary emission source is not located in the breathing zone of the worker - the assessment for this activity involves a primary far-field emission source only (workers are in a control room) |
| | PROC 3,5,8a,8b,9 | Primary emission source located in the breathing zone of the workers (i.e. Within 1 metre) |
| Activity class | PROC 1,3,8a.8b,9 | Transfer of liquid products |
| | PROC 5 | Activities with open liquid surfaces |
| Containment | PROC 1,3,9 | Handling reduces contact between product and adjacent air |
| | PROC 5,8a8b | n/a |
| Localised controls | PROC 1,3,8b, | Vapour recovery systems; LEV |
| | PROC 2,9 | Vapour recovery |
| | PROC 5 | LEV |
| Segregation | PROC 1 | Complete segregation of workers in separate control room |
| Fugitive emission source | PROC 1,3,8b,9 | Process fully enclosed – not breached for sampling |
| | PROC 5,8a | Not fully enclosed – effective housekeeping practices in place. |
| Dispersion | PROC 1, 8a, 8b | Outdoors not close to buildings |
| - | PROC 3 | Outdoors near to buildings |
| | PROC 5,9 | Indoors, any sized room, only good natural ventilation |

List of derived exposure concentrations

| Description of activity | PROC | Physical state of material | Estimated Short-term Exposure Concentrations (mg/m ³) | | Estimated Long-term Exposure Concentration (mg/m ³) | |
|--|------|----------------------------------|---|---|---|---|
| | | | 50 th percentile value | 90 th percentile value | 50 th percentile value | 90 th percentile value |
| Use in closed process, no likelihood of exposure | 1 | Liquid | 8.20 x10 ⁻¹⁰ | 9.30 x 10 ⁻⁰⁹ | 3.60 x 10 ⁻⁰⁹ | 9.40 x 10 ⁻⁰⁹ |

| | 1 | | 05 | 04 | 04 | 04 |
|--------------------------------|----|--------|--------------------------|--------------------------|--------------------------|--------------------------|
| Use in closed batch process | 3 | Liquid | 3.70×10^{-05} | 4.20 x 10 ⁻⁰⁴ | 1.60 x 10 ⁻⁰⁴ | 4.20 x 10 ⁻⁰⁴ |
| (synthesis or formulation) | | | | | | |
| Mixing or blending in batch | 5 | Liquid | 0.0045 | 0.018 | 0.0063 | 0.016 |
| process for formulation of | | 1 | | | | |
| preparations or articles | | | | | | |
| (multistage and/or significant | | | | | | |
| contact) | | | | | | |
| Transfer of substances | 8a | Liquid | 0.002 | 0.023 | 0.0088 | 0.023 |
| from/to vessels/large | | - | | | | |
| containers at non-dedicated | | | | | | |
| facilities (exposure can | | | | | | |
| occur) | | | | | | |
| Transfer of substances | 8b | Liquid | 1.10 x 10 ⁻⁰⁵ | 1.20 x 10 ⁻⁰⁴ | 4.80 x 10 ⁻⁰⁵ | 4.80 x 10 ⁻⁰⁶ |
| from/to vessels/large | | 1 | | | | |
| containers at dedicated | | | | | | |
| facilites | | | | | | |
| Transfer of substance into | 9 | Liquid | 0.00081 | 0.0032 | 0.0011 | 0.0028 |
| small containers (dedicated | | .1 | | | | |
| filling line - vapour/aerosol | | | | | | |
| control) | | | | | | |
| | | 1 | | 1 | 1 | |

List of derived RCRs

| Exposure details | CES | PROC Code | ES 13- 90 th exposure concentrations (mg/m3) | Leading toxic end point / Critical effect | DNEL (mg/m3) | Risk characterisation ratio |
|------------------------------|-------|-----------|--|---|-----------------|-----------------------------------|
| Acute-local effects | CES 2 | PROC 1 | 9.3 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.1 | 9.3 x 10 ⁻⁸ |
| | CES 3 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 4.2 x 10 ⁻³ |
| | CES 4 | PROC 5 | 1.8 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 1.8 x 10 ⁻¹ |
| | CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.1 | 2.3 x 10 ⁻¹ |
| | | PROC 8b | 1.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.1 | 1.2 x 10 ⁻³ |
| | CES 6 | PROC 9 | 3.2 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.1 | 3.2×10^{-2} |
| Long-term – local effects | CES 2 | PROC 1 | 9.4 x 10 ⁻⁹ | Respiratory irritation and corrositivity | 0.05 | 1.9 x 10 ⁻⁷ |
| | CES 3 | PROC 3 | 4.2 x 10 ⁻⁴ | Respiratory irritation and corrositivity | 0.05 | 8.4 x 10 ⁻³ |
| | CES 4 | PROC 5 | 1.6 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 3.2 x 10 ⁻¹ |

| CES 5 | PROC 8a | 2.3 x 10 ⁻² | Respiratory irritation and corrositivity | 0.05 | 4.6 x 10 ⁻¹ |
|-------|---------|------------------------|--|------|------------------------|
| | PROC 8b | 4.8 x 10 ⁻⁶ | Respiratory irritation and corrositivity | 0.05 | 9.6 x 10 ⁻⁵ |
| CES 6 | PROC 9 | 2.8 x 10 ⁻³ | Respiratory irritation and corrositivity | 0.05 | 5.6 x 10 ⁻² |

*Assumes Respiratory Protective Equipment (95% reduction) is worn

Assessment of dermal risk

During the processes that will be carried out for all the exposure scenarios associated with production and use of sulphuric acid a potential risk may arise if sulphuric acid comes into contact with human skin. This is due to the nature of sulphuric acid and its ability to cause chemical burns. As this effect is considered to be related to the corrosivity of sulphuric acid a threshold DNEL cannot be established for this risk and so measures to control this risk should be assessed in a qualitative manner. Though this risk is most pertinent when workers may come into contact with concentrated sulphuric acid in an industrial setting the operational conditions (OCs) and risk management measures (RMMs) used to control and manage the risk of dermal contact events may be equally applicable across all the exposure scenarios.

In the industrial setting an acute risk of dermal burns from exposure to sulphuric acid in its concentrated form (or its dilute form) exists due to possible splashing of the liquid acid. This risk would be highest at times of transfer to tankers, filling of barrels and filling of small vessels etc. Though these events are considered unlikely due to the high degree of system closure and control the risk is still protected against in order to eliminate any possible routes of exposure.

The risk of dermal contact is reduced due to the OC's in place. The specialised nature of the systems and the degree of closure associated with them ensure the potential for dermal contact is minimised. All pipes and transfers lines are closed and sealed in order to reduce possible exposure to leaks or splashes, as are the reactors to reduce possible emissions. During times of transfer to/from road tankers gas displacement lines and special connecting systems are in place to reduce the levels of gaseous emissions that could deposit to surfaces including human skin. Specialised tanker coupling/uncoupling systems and targeted purging systems may be used in certain circumstances where large volumes and high concentrations are required. Training and certification ensures the workers understand the correct procedures for use of these specialized systems so that the measures in place to reduce emissions are conducted so proper function can be maintained.

In addition to the measures in place to reduce system emissions, workers are completely separated from the site of operation. Workers are generally housed in areas segregated from the main emission sources and time spent on tasks which require close proximity to the emission sources can be minimised effectively. Separate control rooms, screens and outdoor reactor units help to keep workers away from any potential sources of exposure. Emergency measures (and training on procedures and safe work practice) are in place in the industrial setting to ensure that any unforeseen events are safely dealt with in the case that they do arise. These measures range from procedural policies which are in place to guide workers in the proper response in the case of splashes or spills to dedicated equipment (such as

emergency showers or spill clean-up kits) which can be used to minimise any effects should unforeseen exposure arise.

Personal protective equipment (PPE) should be supplied to any personnel who may be working in areas where potential emission sources (such as transfer pipes) are located. Suitable PPE that should be used to prevent dermal contact for workers would be acid resistant clothing, helmets, gloves, goggles and boots. The PPE should be properly maintained and certified and should be replaced when required. These measures combined will effectively function to ensure three aspects of safe use. These are, firstly, reduction of potential emissions with specialised systems. Secondly reduction of the potential for exposure of workers by means such as segregation and training and thirdly physical protection of the worker with the use of correct PPE. With the combination of these measures it is considered that the risk of chemical burns to workers is adequately managed.

As mentioned above when the concentration of the sulphuric acid decreases so does the potential for chemical burns to human skin. However the same measures are still in place to ensure that workers, professionals and consumers are protected from risk.

14.4 Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Environmental releases:

In order to work within the boundaries of the ES the following conditions should be met:

- Emission to air after scrubbing less than 205 kg per day
- No emission to the municipal STP
- The industrial WWTP sludge should not be spread to soil
- Wastewater should be fully neutralized
- Measured emissions should be confirmed to be less than the relevant PNECs in section 3.

Worker exposure:

In order to work within the boundaries of the ES the following conditions should be met:

- LEV is in place to capture gaseous emissions and reduce the potential for exposure.
- Workers should wear protective anti-acid gloves, goggles, overalls and boots at all times in the production and transfer area.
- Respiratory equipment should be worn if required.
- Workers should be suitably trained in the correct use of all machinery and PPE used in industrial cleaning.
- Any measured exposure should be confirmed to be less than the relevant DNELs in section 3 above.

| 14.5 | Additional good practice advice beyond the REACH CSA. |
|------|---|
| | |

- Do not eat, drink or smoke when working with sulphuric acid.
- Always wash hands and exposed skin thoroughly after using sulphuric acid or any surfaces/machinery that may have come into contact with sulphuric acid.
- Workers should be suitably trained in all safety procedures and in the safe handling of sulphuric acid to prevent risk of exposure.
- All PPE should be properly maintained and stored in an appropriate way so as not to damage its integrity. Workers should be correctly trained in its use.
- Procedural and safety compliance should be routinely assessed by management
- Machinery should be regularly maintained and checked for proper function
- Efficacy of all emission RMMs and waste treatment procedures should be routinely assessed and confirmed to be functioning correctly