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

1.1. Product identifier:

Trade name: CONCENTRATED SULPHURIC ACID

IUPAC name: sulphuric acid

UN No.: 1830

CAS No.: 7664-93-9

EC No.: 231-639-5

Index No.: 016-020-00-8

Registration No.: 01-2119458838-20-0041

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

Identified uses:

As solvent for phosphate dissolution. For production of colorants, softeners and surfactants (tensides). As electrolyte (battery acid) in lead batteries. Sulphuric acid is one of the key primary raw materials in chemical and cellulose and paper industries.

Uses advised against: the product may not be generally available.

1.3. Details of the supplier of the material safety data sheet:

Manufacturer identification: KGHM Polska Miedź S.A.
Oddział Huta Miedzi „Legnica”
Złotoryjska 194
59-220 Legnica

Telephone numbers:

Head of Sulphuric Acid Division: (48 76) 747 55 01 – available from Monday to Friday between 7.15 AM and 3.15 PM

Head of Customer Service Unit and Finished Product Warehouse: (48 76) 747 28 00 - available from Monday to Friday between 7.15 AM and 3.15 PM

Facsimile: (48 76) 747 20 05

Person responsible for material safety data sheet: (48 76) 747 22 45 / e-mail:

karty.charakterystyki@kgbm.pl

1.4. Emergency telephone numbers:

(48 76) 747 50 02 – manufacturer’s emergency telephone number available 24h/day

112 (general emergency), **998** (fire department), **999** (emergency ambulance service)

SECTION 2. Hazard Identification

2.1. Classification of the substance:

Classification according to Regulation No. 1272/2008 (CLP):

Skin corr. 1A; H314: causes severe skin burns and eye damage;

2.2. Label elements:

GHS 05



Signal word: „DANGER”

Hazard Statements (H):

H314 – causes severe skin burns and eye damage.

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Precautionary statements (P):

- P201** – Obtain special instructions before use.
- P307+314** – Get medical advice/attention if you feel unwell.
- P281** – Use personal protective equipment as required.
- P405** – Store locked up.
- P273** – Avoid release to the environment.
- P501** – Dispose of contents/container to the product producer

2.3 Other hazards

Oxidising, corrosive and hazardous to the environment substance. Causes deep burns in contact with skin or eyes. Inhalation of vapours and aerosols of substance leads to severe damage to the respiratory tracts (EL=1 g/m³, STEL=3 g/m³). Ingestion leads to severe burns of oral cavity, gullet and stomach – may cause stomach perforation.

Contact with flammable materials may cause fire.

Concentrated sulphuric acid damages multiple organic substances, in particular organic fabrics and textiles. Releases large volumes of heat while diluting (add acid to water). Pouring water to the concentrated sulphuric acid may result in explosion. Reactions with any and all alkalis and alkaline substances are particularly rapid and may even lead to explosion. It displaces salts of the other acids in contact with them, frequently leading to explosions (e.g. chlorine oxyacids) or release of poisonous gases (e.g. hydrogen chloride from sodium chloride). While reacting with vast majority of metals, sulphuric acid (VI) releases hydrogen or SO_x. In case of release to aqueous environment, the substance causes reduction of its pH which can lead to death of fish, plants and invertebrates. Due to corrosive properties, the substance is hazardous for organisms and micro-organisms living in soil.

Other hazards not classified: none

SECTION 3. Composition and information on ingredients

3.1. Substances:

a) according to the Regulation No. 1272/2008 (CLP):

Composition and information on ingredients	Percentage content	Symbols	H statements
<p style="text-align: center;">H₂SO₄ CAS No.: 7664-93-9 EC No.: 231-639-5 Index No.: 016-020-00-8</p>	> 94.0% w/w	Skin corr 1A	314
<p style="text-align: center;">H₂O CAS No.: 124-38-9 EC No.: 204-696-9</p>	≤ 6.0% w/w		

3.2. Mixtures:

n/a

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SECTION 4. First aid measures

4.1 Description of first aid measures:

Respiratory ways: move the exposed person away from the place of exposure, ensure fresh air and calmness (rest in a semi-sitting or sitting position). Physical effort may cause lung oedema. Protect against heat loss. Immediate medical attention required.

Poisoning by ingestion: rinse oral cavity, serve water for drinking. Avoid vomits (risk of perforation), do not attempt neutralisation. Immediate medical attention required.

Eye contact: rinse with plenty of running water (preferably) with eyelid pulled away from eye for app. 15 minutes. Protect healthy eye, remove contact lenses. Immediate medical attention required.

Skin contact: remove contaminated clothing immediately, wash skin with plenty of water, preferably running water. Apply aseptic dressing. Medical attention required.

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

Long-term exposure to mists or vapours may cause chronic conjunctivitis, chronic bronchitis, nosebleeds and tooth enamel damage. Long-term exposure to mists containing sulphuric acid may cause neoplastic lesions.

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

The undertakings using sulphuric acid employing no in-house medical rescue service should provide the following drugs in near vicinity of workplaces: oxygen, atrovent in capsules for inhalation. In the case of skin contact, administer polyethylene glycol 400.

In case of dyspnea (breathlessness) administer oxygen, preferably using a mask. If the exposed person experiences hoarseness, wheezing, inability to speak, choking – administer atrovent in capsules for inhalation. Medical attention necessary. In case of unconsciousness, place and transport the exposed person in the recovery position. Apply resuscitation, if necessary.

Availability of emergency showers in a vicinity of workplaces is necessary.

SECTION 5. Firefighting measures

5.1. Extinguishing media:

Suitable extinguishing media: non-flammable substance. Use the extinguishing media depending on the materials stored in-house. In case of fire in direct vicinity, use extinguishing media suitable for the materials under fire. Use water in case of no acid leakage. In case of acid leakage – use carbon dioxide and extinguishing powders.

Unsuitable extinguishing media: large volume of heat is released in contact with water (splashing risk).

5.2. Special hazards arising from the substance:

Fire causes releases of hazardous gases: SO_x. Hydrogen is released in contact with metals (explosion hazard). Sulphuric acid produces dense mist in contact with water.

5.3. Advice for fire-fighters:

Personnel involved in fire extinguishing should be equipped in respiratory protection. Removal of substance should be carried out using respiratory protection equipment and protective clothing (gas-proof).

General recommendations: notify the others on fire. Remove all persons not involved in fire extinguishing from the hazardous area. Notify the Senior Shift Supervisor of the Smelter and Refinery.

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SECTION 6. Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures:

Remove all persons not involved in rescue action from the area. Use personal protection equipment as stated in Section 8.

6.2. Environmental precautions:

Avoid releasing the product to the environment.

Protect against direct release to the sewage system, surface and groundwater. Protect against spreading.

6.3. Methods and material for containment and cleaning up:

Highly diluted acid should be neutralized with sodium bicarbonate or sodium carbonate (baking soda) – premises should be well ventilated due to carbon dioxide release. Rinse with plenty of water. Acid of higher concentrations should be neutralized with hydralime. Large volumes of collected and neutralized mass should be disposed as special waste of hazardous properties.

6.4. Reference to other sections:

Information on personal protective equipment is provided in Section 8, waste handling described in Section 13.

SECTION 7. Handling and storage

7.1. Precautions for safe handling:

7.1.1. Work in well-ventilated premises. Protect containers and packaging containing the substance against physical damage. Protect against direct exposition to sunlight, heat, water and other unsuitable materials. When diluting, always add acid to water and never the reverse. While opening metal containers, use non-sparking tools due to potential presence of hydrogen. Empty acid containers may be hazardous, since these may contain product residues in a form of vapour.

7.1.2. Do not eat and drink while using. Avoid contact with substance, avoid inhalation of vapours and mist, observe personal hygiene rules, apply personal protection equipment according to Section 8. Wash hands after using and remove clothing and protection equipment before entering the eating areas.

7.2. Conditions for safe storage, including any incompatibilities:

Sulphuric acid solutions should be stored (warehoused) in specially adjusted tanks or containers. Warehouse tank should be equipped with an upper vent due to possible accumulation of hydrogen produced in reaction with steel sheet. The tanks should be placed on acid-proof flooring.

The tanks containing sulphuric acid should be made of acid-proof materials, including: steel, acid-proof steel, high density polyethylene. The area of warehouse should have acid-proof floor included towards drop inlets and available sewage system.

7.3. Specific end use(s):

Identified uses are listed in Section 1.2.

SECTION 8. Exposure control/personal protection

8.1. Control parameters:

Occupational exposure limit values to be controlled:

In a form of mist:

EL 1 mg/m³

STEL 3 mg/m³

TEL not determined

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BEL	not determined
In a form of thoracic fraction:	
EL	0.05 mg/m ³
STEL	not determined
TEL	not determined
BEL	not determined

Thoracic fraction – a respirable aerosol fraction entering the lungs' airways and posing a hazard to health upon depositing in thoracic and bronchial as well as gas exchange area.

Additional notes:

Ordinance of the Minister of Labour and Social Policy of 29 November 2002 on the occupational exposure limit values (Journal of Laws 02.217.1833 as amended)

Ordinance of the Minister of Health of 30 December 2004 on health and safety of work related to presence of chemical agents in the workplace. (Journal of Laws 05.11.86 as amended);

Determination in air at the workplace:

PN-79/Z-04056 sheet 03 Air Purity Protection. Determination of sulphuric acid content. Determination of workplace sulphuric acid using the titration method

PN-91/Z-04056 sheet 02 PN-Z-04008-7.2002. Air Purity Protection – Air sampling – Principles of workplace atmosphere sampling and interpretation of results;

PN-EN 689:2002 Workplace atmospheres. Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values;

PN-EN 482:2006 Workplace atmospheres. General requirements for the performance of procedures for the measurement of chemical agents;

PN ISO 4225/Ak:1999 Air quality -- General aspects -- Vocabulary (national sheet);

8.2. Exposure controls.

At the determined and known substance concentration, the personal protection equipment should be selected with a view to concentration of substance present at a given workplace, exposure period, activities performed by the worker and PPE manufacturer's recommendations.

In emergency situations or when concentration of substance at the workplace is unknown, use PPE isolating the body (gas-proof overalls combined with isolating respiratory protection equipment).

Eye/face protection: goggles protecting against liquid droplets (for half-masks).

Hand/foot protection: mandatory – polyvinyl chloride gloves and shoes

Skin protection: protective clothing made of viton, butyl rubber or hypalon-coated materials.

Respiratory protection: mask or half-mask with B-P2 class combination filter. In the case of insufficient oxygen content in atmosphere (concentration below 17% vol.) or concentration of sulphuric acid above 1% vol., use autonomous or stationary isolating equipment.

Hygiene measures: change contaminated clothing immediately. Wash contaminated clothing before use. Wash hands and face after contact with the product. Do not eat and drink while working with the product.

SECTION 9. Physical and chemical properties

9.1. Information on basic physical and chemical properties:

Appearance: colourless liquid (20°C)

Odour: odourless

Odour threshold: n/a

pH: strong acid

Melting point: -13.89 to -10 °C for 96% acid

Boiling point: app. 330°C for 96% acid

Flash point: n/a

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Ignition temperature: n/a**Evaporation rate:** no data**Flammability:** n/a**Explosive limits:** n/a**Vapour pressure:** 6 Pa for 90% acid (20°C)**Vapour density:** no data**Relative density:** app. 1.8355 g/cm³ (20°C) for 96% acid**Solubility:**

in water (20°C): soluble (note! large amount of heat released)

in acids (20°C): depending on acid and concentration

in alkalis (20°C): insoluble

in organic solvents (20°C): no data

Partition coefficient n-octanol/water: n/a**Ignition temperature:** n/a**Decomposition temperature:** no data**Viscosity:** 22.5 cP (20°C) for 96% acid**Explosive properties:** n/a**Oxidising properties:** able to increase oxidation rate of reacting chemical compounds**9.2. Other information:**None.

SECTION 10. Stability and reactivity

10.1. Reactivity: Corrosive. Chemically active compound. Product has no explosive or pyrophoric properties, however the reactions may be of rapid and explosive nature. Reactions with metals lead to intensive release of hydrogen, which forms explosive mixtures with atmosphere.

10.2. Chemical stability: Sulphuric acid is stable in normal conditions of use and storage.

10.3. Possibility of hazardous reactions: Concentrated solutions react rapidly with water, splashing and releasing heat and corrosive vapours. Reaction with carbonates leads to production of carbon dioxide. Toxic hydrocyanic acid and hydrogen sulphide are produced in reactions with cyanides and sulphides, respectively). Reactions with metals cause intensive hydrogen release.

10.4. Conditions to avoid: Heat, humidity, low temperatures.

Protect against direct exposition to sunlight, heat, water and other unsuitable materials. When diluting, always add acid to water and never the reverse.

10.5. Incompatible materials: Water, potassium chlorate, potassium perchlorate, potassium, sodium, lithium permanganate, alkalis, organic materials, halogens, metal acetylides, oxides, hydrides (metals (hydrogen release), strongly oxidising and reducing substances and many other reactive substances.

10.6. Hazardous decomposition products: Toxic vapours of sulphur oxides upon heating to the decomposition point are produced. While reacting with water or vapour, toxic and corrosive vapour are produced. Reaction with carbonates leads to production of carbon dioxide. Toxic hydrocyanic acid and hydrogen sulphide are produced in reactions with cyanides and sulphides, respectively).

SECTION 11. Toxicological information

11.1. Information on toxicological effects:

a) acute toxicity: based on available data, the classification criteria are not met.

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Lethal and toxic concentrations and doses:LD₅₀ (orally, rat): 2140 mg/kgLC₅₀ (rat, inhalation): 375 mg/m³LD₅₀ (rabbit, rat, skin): no datab) Skin corrosion/irritation:

Sulfuric acid(VI) is listed in harmonized classification and labelling of hazardous substances (table 3.1. from appendix VI of CLP) and classified as:

Skin Corr. 1A; H314 - causes severe skin burns and eye damage.

c) Serious eye damage/ eye irritation:

based on available data, the classification criteria are not met.

d) Respiratory tract or skin sensitization:

based on available data, the classification criteria are not met.

e) Germ cell mutagenicity:

based on available data, the classification criteria are not met.

f) Carcinogenicity:

based on available data, the classification criteria are not met.

g) Reproductive toxicity:

based on available data, the classification criteria are not met.

h) Specific target organ toxicity — Single exposure:

w based on available data, the classification criteria are not met.

i) Specific target organ toxicity — Repeated exposure:

based on available data, the classification criteria are not met.

j) Aspiration hazard:

based on available data, the classification criteria are not met.

Other information:

Information on the potential exposure routes, symptoms related to product properties and possible product exposure effects are described in Section 4.2.

11.2. Information on the potential exposure routes:

Absorption routes: respiratory tracts, digestive system, skin/eye contact.

11.3. Delayed, direct and chronic effects of single and long-term exposure:

Detailed information on the symptoms related to product properties and possible product exposure effects are described in Section 4.2.

SECTION 12. Ecological information

12.1. Toxicity:

Based on available data, the classification criteria for environmental hazards are not met.

Toxic concentration of sulphuric acid for aqueous animal and plant organisms:LC₅₀/96 h fish: *Lepomis macrochirus* – 16 mg/l,NOEC/65d fish: *Jordanella floridae*– 0.025 mg/l,EC₅₀/48h crustaceans: *Daphnia magna* – 100 mg/l,NOEC crustaceans: *Tanytarsus dissimilis* – 0.15 mg/l,NOEC/72h algae: *Desmodesmus subspicatus* – 100 mg/l,

12.2. Persistence and degradability: Persistent substance. Reacts with soil components forming sulphates or decomposes to SO₂.

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12.3. Bioaccumulative potential: The product has low bioaccumulative potential.

12.4. Mobility in soil: Vein soil. Mobility increases proportionally to dilution. While penetrating soil, it dissolves soil components, in particular these containing carbonates. It reacts with organic substances and soil fertilizers. Dissolves in water in any quantity. Upon release to soil, it may be infiltrated down to groundwater.

12.5. Results of PBT and vPvB assessment: not applicable to inorganic substances.

12.6. Other adverse effects: no data.

SECTION 13. Disposal considerations

13.1. Waste treatment methods.

Do not dispose of to any sewage system. Prevent contamination of surface and ground waters and soils. Do not dispose of at municipal landfills. Consider re-use. Carry out recovery or disposal in compliance with applicable legislation in force.

Waste management should be carried out pursuant to the Act of 14 December 2012 on waste (Journal of Laws of 2013, No. 0, item 21).

Recommended method of neutralization of waste: Physical and chemical transformation. Neutralization with calcium or sodium carbonates or hydralime water suspension..

SECTION 14. Transport information

14.1. UN number: 1830

14.2. UN proper shipping name: SULPHURIC ACID containing more than 51% of acid.

14.3. Transport hazard class(es): RID/ADR: 8

14.4. Packing group: RID/ADR: II

14.5. Environmental hazards: The substance is not classified as environmentally hazardous.

14.6. Special precautions for users: Avoid direct contact with the substance. Personal protection equipment is described in Section 8.2.2.

In case of leakage, acid collected in land depressions and hollows should be pumped out into an acid-proof container and the remains should be neutralized with milled calcium carbonate, dolomite and collect in an acid-proof container for further utilization. Treat any post-neutralization mass collected along with soil as hazardous waste. Neutralize the treated land surface with 10% hydralime suspension. Wash the treated surface with plenty of water.

14.7. Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code: n/a.

SECTION 15. Regulatory information

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

The substance is included in the list of category 3 precursors referred to in the Regulation (EC) No 273/2004 of the European Parliament and of the Council of 11 February 2004 on drug precursors (OJ EC L 047 of 18.02.2004 as amended).

Legislation:

Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC as amended; Act of 27 April 2001 – Environmental Protection Law (Journal of Laws 01.62.627 as amended); Act of 25 February 2011 on chemical substances and mixtures thereof (Journal of Laws 2011.63.322 as amended); Act of 14 December 2012 on waste (Journal of Laws 2013.0.21 as amended); Ordinance of the Minister of Environment of 27 September

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2001 on waste catalogue (Journal of Laws 01.112.1206 as amended); Act of 11 May 2001 on packaging and packaging waste (Journal of Laws 01.63.638 as amended); Act of 19 August 2011 on transport of hazardous goods (Journal of Laws 2011.227.1367 as amended); Ordinance of the Minister of Economy of 21 December 2005 on the essential requirements for personal protection equipment (Journal of Laws 2005.259.2173 as amended); Ordinance of the Minister of Health of 2 February 2011 on testing and measurements of agents hazardous to health in working environment (Journal of Laws 11.166.2526 as amended); Ordinance of the Minister of Economy of 29 January 2013 on the restrictions to manufacturing, trading or use of hazardous or potentially hazardous substances and mixtures and placing on the market or use of products containing such substance or mixtures (Journal of Laws of 2013, item 180 as amended); Ordinance of the Minister of Environment of 28 January 2009 amending the Ordinance on the conditions to be met for releasing wastewater to water or soil and on substances particularly hazardous to the water environment (Journal of Laws 2009.27.169 as amended)

15.2. Chemical safety assessment:

The following chemical safety assessment was carried out for the product: 'Chemical Safety Report' for sulphuric acid is available at KGHM Polska Miedź S.A. Legnica Copper Smelter and Refinery.

SECTION 16. Other information

Explanation of abbreviations and acronyms used in the safety data sheet:

CAS Number – a numeric identifier assigned to each chemical substance by the US organization - Chemical Abstracts Service (CAS) and enabling its identification.

EC Number – a number assigned to a chemical substance in the EINECS - European Inventory of Existing Chemical Substances or a number assigned to a substance in the ELINCS - European List of Notified Chemical Substances or a number assigned in a list of chemical substances included in the "No-longer polymers" publication.

Index Number – an identification code provided in Part 3 of Annex VI to the Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures.

Registration Number – a number assigned by the European Chemicals Agency (ECHA) upon registering the substance/semi-product by the manufacturer/importer pursuant to the REACH Regulation.

LD₅₀ – a dose of toxic substance expressed in milligrams per kg of body mass necessary to kill 50% of a studied population

LC₅₀ – concentration of a substance present in the inhaled air expressed in mg/l, causing death of 50% of the studied population upon a specified period of inhalation.

EC₁₀ – a dose of substance expressed in mg/l, causing a specific pharmacological effect (i.e. growth inhibition) in 10% of the studied population in a specified period of time.

NOEC – no observed effect concentration – means the highest tested concentration at which, no adverse effect is observed.

EL – Exposure Limit – average weighted value of concentration, exposure of the worker to which during the 8-hour and average weekly working time referred to in the Labour Code, for the entire period of its occupational activity, should cause no adverse effects to its health condition and health condition of its future generations.

STEL – Short-Term Exposure Limit – average value of concentration, which should cause no adverse effects to health condition of the worker, if present in the working environment for the period not exceeding 15 minutes and 2 times during a shift at the latest, in at least 1 hour intervals

DNEL – derived no-effect level.

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PNEC – predicted no-effect concentration

Necessary training: job position training in safe use of substances considering its hazardous properties for human and harmful properties for the environment.

Source of information used in this safety data sheet:

- Own results of quantitative and qualitative analyses.
- Hazardous Substances. A practical guide of ALFA-WEKA
- European Chemical Substance Information System.
- Encyklopedia Techniki CHEMIA. (*Encyclopaedia of Technique. CHEMISTRY*), WNT
- *CHEMISTRY, structure and reactions*. Milton K. Snyder
- Chemical Safety Report

All data are based on our best knowledge. The recipients of our product must follow the existing legislation and other regulations currently in force.

This safety data sheet is the property of KGHM Polska Miedź S.A. Legnica Copper Smelter and Refinery and is intended for KGHM product only.

Changes in content of the safety data sheet:

- SECTION 3. Composition/information on ingredients

Further information available at: telephone numbers listed in Section 1

Prepared by: Deputy Chief Process Safety Specialist, Hubert Opaczewski, M. Sc. in Engineering