Aquatrade Water Treatment Chemicals (Pty) Ltd



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Reg No: 2015/060029/07 Vat No: 4610268676

Identification

GHS Product Identifier

AQT 124

Other means of identification

| CAS: | Not listed in registry |
|-----------------------|---------------------------|
| EC: | Not listed in registry |
| RTECS: | Not listed in registry |
| ICSC: | Not listed in registry |
| Chemical Family: | Oxidising Biocide |
| Synonyms: | Chlorine Dioxide Solution |
| Proper Shipping Name: | CORROSIVE LIQUID, N.O.S. |
| Chemical Formula: | Mixture |

Recommended use of the chemical and restriction on use

Oxidising Biocide for industrial water treatment. The residual levels of chlorine (hypochlorite ion and hypochlorous acid), chlorine dioxide, chlorate ion, chloramine and disinfection by-products shall be monitored in the finished drinking water to ensure compliance to all applicable regulations and with a residual of 1 ppm as free chlorine.

Supplier's details

AQUATRADE WATER TREATMENT CHEMICALS (PTY) LTD

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Spilltech: +27 861 000 366 (Available 24/7)

2 Hazard(s) identification

Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008

Acute Toxicity - Inhalation (Category 4), H332 Skin Corrosion/Irritation (Category 2), H315 Serious Eye Damage/Irritation (Category 2), H319 Acute Aquatic Toxicity (Category 2), H401

For the full text of the H-Statements mentioned in this Section, see Section 16.

GHS label elements

Warning



Causes skin irritation

Causes serious eye irritation

Harmful if inhaled

Toxic to aquatic life

Wash thoroughly after handling.

Use only outdoors or in a well-ventilated area.

Wear protective gloves/protective clothing/eye protection/face protection.

IF ON SKIN: Wash with plenty of soap and water.

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

If skin irritation occurs: Get medical advice/attention.

IF eye irritation persists: Get medical advice/attention.

Take off contaminated clothing and wash it before reuse.

In case of fire: Use water to extinguish.

Store locked up.

Dispose of contents and container in accordance with local, regional, national, international regulations.

Other hazards which do not result in classification

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

3 Composition/information on ingredients

| Description | CAS Number | EINECS Number | % | Note |
|-----------------------------------|------------|------------------|---|--------------------------------------------------------------------------|
| Confidential Business Information | | | 0 | Information available to Emergency Responders on Tel: +27 82 921 0643 |

4 First-aid measures

Description of necessary first-aid measures

Eyes:

If symptoms develop, move patient away from the source of exposure and into fresh air. Flush eyes gently with large amounts of water while holding eyelids apart. If symptoms persist or there is any visual difficulty, seek medical attention.

Skin:

Concentrated solutions of the material (> 1000 ppm) may be highly irritating, especially on prolonged contact. Remove contaminated clothing immediately. Immediately flush exposed skin with large amounts of water. Wash thoroughly with mild soap. Consult a physician if irritation or burning persists. Contaminated clothing must be laundered before re-use. Lower concentrations (<1000) ppm may cause some irritation with very-prolonged exposure.

Ingestion:

First aid is not normally required when small amounts of the material are ingested. If symptoms develop or if large amounts of material have been ingested, **DO NOT** induce vomiting. **DO NOT** give anything by mouth if the patient is unconscious. Drink large quantities of water. Consult a physician immediately. Neutralization and use of activated charcoal are not recommended.

Inhalation:

If symptoms develop, immediately move individual away from exposure and into fresh air. Seek immediate medical attention; keep person warm and quiet. If person is not breathing, begin artificial respiration. If breathing is difficult, administer oxygen. Monitor the patient closely for delayed development of pulmonary edema, which may occur up to 72 hours after inhalation.

Most important symptoms/effects, acute and delayed

Causes skin and eye irritation. Harmful if inhaled.

Indication of immediate medical attention and special treatment needed, if necessary

Call poison control center or doctor for treatment advice.

5 Fire-fighting measures

Suitable extinguishing media

Extinguishing media:

Water is recommended since chlorine dioxide is soluble in water and the toxic effects are reduced on dilution.

Unsuitable extinguishing media:

None known.

Specific hazards arising from the chemical

General Hazard:

In large fire fuelled by other materials this product may decompose.

Hazardous combustion products:

May form chlorine, hydrochloric acid gas, oxygen on combustion or decomposition.

Unusual Fire and Explosion Hazards:

There are no special fire hazards known to be associated with the material.

Flash Point:

Not applicable

Auto-ignition Temperature:

Not applicable

Explosive Limit:

Chlorine dioxide solution is not explosive. Chlorine dioxide gas, which may evolve from chlorine dioxide solution, may spontaneously decompose with a mild energy release at concentrations of 10% in air or greater at standard temperature and pressure (i.e., 76 mm Hg partial pressure).

Chlorine dioxide gas may explode with violent force at concentrations of 30% or greater in air at standard temperature and pressure (i.e., 228 mm Hg partial pressure).

Special protective actions for fire-fighters

Wear a self-contained breathing apparatus (SCBA) with a full face piece operated in the "positive pressure demand" setting. Use SCBA in conjunction with appropriate chemically resistant personal protective gear. Refer also to the personal protective equipment section of this SDS

6 Accidental release measures

Personal precautions, protective equipment and emergency procedures

If run-off occurs, notify proper authorities of any runoff, as required. Persons not wearing protective equipment should be excluded from area of spill until clean-up has been completed.

Environmental precautions

Environmental cleanup procedures:

Contain the spill with sand, clay or earth and dilute with large amounts of water before disposal. Contact expert assistance in the event of major releases. **DO NOT** return product to container or tank due to risk of decomposition. Inform the local emergency services. **DO NOT** allow material to contaminate ground water system.

Methods and materials for containment and cleaning up

Large spills:

Prevent runoff to sewers, streams, lakes or other bodies of water.

Small spills:

Absorb liquid on vermiculite, floor absorbent or other absorbent material. Flush area with water. Stop spill at source, dike area around spill to prevent spreading, and pump liquid to salvage tank. Remaining liquid may be taken up on sand, clay,

earth, vermiculite, floor absorbent, or other absorbent material and shoveled into containers. Flush with water the area from which the bulk of the spill has been removed.

7 Handling and storage

Precautions for safe handling

Avoid inhalation and skin contact. Ensure necessary ventilation in work areas in which chlorine dioxide solution is being used. Use local exhaust ventilation at point of vapour emissions. Ensure that gas masks/gas filters are available. Ensure that emergency shower facilities are available. Avoid contact with the following chemicals and materials: iron, copper and their alloys, reducing agents.

In order to prevent the evolution of chlorine dioxide gas into the breathing zones of workers, agitation of the material should be minimized, and the material should not be stirred, mixed turbulently, sprayed or splashed.

Conditions for safe storage, including any incompatibilities

The material should be stored indoors, only in the containers in which it is shipped, or in containers authorized by the manufacturer for such storage. Storage temperatures should be maintained above 10° C and below 44°C. The material should not be stored outside or exposed to direct sunlight or freezing temperatures (0°C or below). The material should not be heated to temperatures in excess of 60°C. At temperatures above 60°C, the gas concentration in the headspace of the container may reach high, energetically unstable concentrations.

SANS 10263-0 Warehousing

- **8.4.3.2** Where flammable or **corrosive** substances are stored, the floor shall slope away from the storage area (primary collection area) to a secondary catch basin or sump of capacity at least 10 % of the total available storage volume of the fire section concerned. The secondary catch basin shall be within the fire section, and shall be such that it can be well ventilated. Care shall be taken in the design of such areas to prevent contamination of the soil or ground water.
- **9.7.2** Every type of storage area inside a warehouse shall be clearly demarcated, for example separate storage areas for poisons, flammables and **corrosives** shall display the relevant hazard class diamond (see table 1). The dimensions of the hazard class diamonds shall be at least 250 mm x 250 mm.
- 12.8.5 Storage of flammable liquids of class 3, toxic substances of division 6.1 and corrosives of class 8

Nitro-methane class 3, UN No. 1261, shall be separated from substances of class 6.1, and cyanides of division 6.1 shall be separated from acids of class 8. Concentrated acids and bases shall be segregated by at least 1 m. Packaged flammable liquids of class 3, toxic substances of division 6.1 and corrosives of class 8 that are of category 3 can be stored in the same area, provided that

- a) they are kept above floor level, and
- b) liquid dangerous goods of one class are not stored above dangerous goods of another class.
- **12.8.8.4 Corrosives** (see class 8 in SANS 10228) that leak or spill from their packaging can cause serious damage to other packages, with potentially hazardous consequences.

Corrosives shall be segregated from toxic substances, infectious substances, aerosols, flammables, oxidizing substances and organic peroxides.

The provisions of above apply to the storage of the following quantities of dangerous goods.

| Corrosives (acids and bases)Class 8 | | |
|-------------------------------------|------------|--|
| Category 1 | > 50 kg | |
| Category 2 | > 200 kg | |
| Category 3 | > 1 000 kg | |

8 Exposure controls/personal protection

Control parameters

The OSHA permissible exposure limit (PEL) for ClO2 gas in air is 0.1 ppm (0.3 mg/m3) as an 8-hour time weighted average.

NIOSH recommended exposure limits (REL) and ACGIH threshold limit values (TLV) are also 0.1 ppm.

NIOSH and ACGIH short-term exposure limits (STEL) are 0.3 ppm (0.83 mg/m3) for periods not to exceed 15 minutes. The STEL concentration should not be repeated more than 4 times per day and should be separated by intervals of at least 60 minutes.

Exposure Guidelines (vapor)

OSHA PEL 0.100 ppm - TWA **ACGIH TLV** 0.100 ppm - TWA **ACGIH TLV** 0.300 ppm - STEL

0.28 mg/m3 / 0.1 ppm (8 hr), 0.84 mg/m3 / 0.3 ppm (15 min); Finland (HTP):

0.8 mg/m3 / 0.1 ml/m3 (TRGS 900 limit); France (VLR): Italy (ACGIH): 0.1 ppm (8-hr TWA), 0.3 ppm (15 min STEL);

Netherlands (MAC): 0.3 mg/m3 / 0.1 ppm (STEL); 0.3 mg/m3 / 0.1 ppm (TLV); Norway:

0.28 mg/m3 / 0.1 ppm (8 hr VLA-ED), 0.84 mg/m3 / 0.3 ppm (15-min VLA EC); Spain:

0.3 mg/m3 / 0.1 ppm (NGV), 0.8 mg/m3 / 0.3 ppm (TGV); Sweden:

UK (WEL): 0.28 mg/m3 /0.1 ppm (8-hr TWA), 0.84 mg/m3 / 0.3 ppm (STEL).

Appropriate engineering controls

Provide sufficient mechanical ventilation, general and/or local exhaust, to maintain exposure below allowable limits.

Avoid spraying the material. Supply safety shower and eyewash in immediate vicinity of exposure area. Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.

Individual protection measures

The selection of PPE is dependent on a detailed risk assessment. The risk assessment should consider the work situation, the physical form of the chemical, the handling methods, and environmental factors. Recommendations below is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.













Eye/face protection:

Face shield and safety glasses or safety goggles. Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166 (EU). Contact lenses should not be worn; they may contribute to severe eye injury.

Skin protection:

Handle with gloves made of butyl rubber, neoprene or PVC. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands. The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves.

Body Protection:

Complete suit protecting against chemicals made of polyester or acrylic. Wash contaminated clothing before reuse. Emergency showers or baths must be made available. The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection:

Exposures in the workplace should be monitored to determine if worker exposure exceeds the facilityspecified exposure "action level" or the use of the material produces adverse health effects or symptoms of exposure. Provide adequate ventilation to maintain all work areas at concentrations below 0.1 ppm chlorine dioxide concentration. If the generation of

vapors or mists is possible, use local ventilation. Where gas concentration may exceed 0.1 ppm, only a NIOSH/MSHA approved full face acid gas respirator should be used. Monitoring results must be used to assess the proper level or respiratory protection necessary. Proper engineering and/or administrative controls should be used to reduce worker exposure. The facility's respiratory protection program must meet the requirements established in 29 CFR 1910.134, which includes a program for medical evaluation. A NIOSH/MSHA approved self-contained breathing apparatus, with full face piece, is required for leaks and emergencies where the concentration may exceed 5 ppm.

9 Physical and chemical properties

Physical and chemical properties

| Appearance (physical state, colour etc): | Clear yellow liquid |
|-----------------------------------------------|--------------------------------|
| Odour: | Chlorine like pungent odour |
| Odour threshold: | 0.1 ppm |
| pH: | 3 - 4 |
| Melting/Freezing Point: | No test data available/0° C |
| Initial boiling point and boiling range: | 100° C/No test data available |
| Flash point: | Do not flash |
| Evaporation rate: | No test data available |
| Flammability (solid, gas): | Not flammable |
| Upper/lower flammability or explosive limits: | Not flammable or explosive |
| Vapour pressure: | No test data available |
| Vapour density: | No test data available |
| Relative density: | 1.00 - 1.01 |
| Solubility(ies): | Miscible in water |
| Partition coefficient: n-octanol/water: | No test data available |
| Auto-ignition temperature: | No test data available |
| Decomposition temperature: | No test data available |
| Viscosity: | 0.894 cP (centipoise) at 25 °C |

NOTE: The physical data presented above are typical values and should not be construed as a specification.

10 Stability and reactivity

Reactivity

Material is not reactive under normal conditions of storage and use.

Chemical stability

The material, as solution, is stable in the dark. On exposure to light, the solution may decompose to an aqueous solution of chloride and chlorate ions. In regard to vapor (gas) that may evolve from the material, see "Hazardous Decomposition Products" below.

Possibility of hazardous reactions

Material does not undergo hazardous polymerization.

Conditions to avoid

Storage temperatures should be maintained above 10° C and below 44° C. The material should not be heated to temperatures in excess of 60° C.

Incompatible materials

Avoid exposure to light. **Avoid** contact with: metals, reducing agents, strong oxidizing agents, sulfur compounds or sulfur-containing components, carbon monoxide, excessive heat, mercury, organic materials, phosphorus.

Hazardous decomposition products

Gas-phase vapors that evolve from the material may decompose on exposure to light, on contact with incompatible materials (see below), or spontaneously at concentrations above 10% in air at standard temperature and pressure (76mm Hg). On decomposition, material may form: Chlorine, hydrochloric acid gas and oxygen.

11 Toxicological information

Toxicological (health) effects

Chlorine dioxide gas is a mucous membrane and respiratory tract irritant. Primary routes of exposure include ingestion, skin and eye contact and inhalation of vapors which may evolve from the material.

Target Organ Effects

This material may cause mild eye irritation; it is unlikely to cause serious eye irritation or injury.

Digestive Tract

This material may cause nausea, vomiting and diarrhea; it is unlikely to cause serious digestive tract injury. Chlorine dioxide given daily in drinking water at 1 - 100 ppm caused a decrease in blood glutathione, altered the morphology of erythrocytes, and caused osmotic fragility in laboratory animals.

Respiratory Tract

The fumes from this material may cause respiratory tract irritation, wheezing and difficulty breathing. In extreme cases, it may cause pulmonary damage and death.

Developmental/Reproductive Effects

Available information is insufficient to assess risk to the fetus from maternal exposure to this material during pregnancy. Chlorine dioxide did not cause birth defects in laboratory animals even at very high exposure levels.

Cancer Effects

Available information is insufficient to assess cancer risk (i.e., carcinogenicity) associated with exposure to this material. This material is not listed as a carcinogen by the International Agency for Research on Cancer (IARC), the National Toxicology Program (NTP), or the Occupational Safety and Health Administration (OSHA) United States Environmental Protection Agency (EPA) or American Conference of Industrial Hygienists (ACGIH).

Other Health Effects

No data available on other possible health effects.

Data for Chlorine Dioxide

Acute Toxicity

Workers - Hazard via inhalation route

Systemic effects

Long term exposure

Hazard assessment conclusion:no hazard identified

Acute/short term exposure

Hazard assessment conclusion:no hazard identified

DNEL related information

Local effects

Long term exposure

Hazard assessment conclusion:DNEL (Derived No Effect Level)Value:0.304 mg/m³Most sensitive endpoint:repeated dose toxicity

DNEL related information

DNEL derivation method: other: To describe the ClO2 uptake in the respiratory tract, the gas categorization scheme of EPA (EPA/600/8-90/066F, October 1994) was used. This scheme separates gases into three categories based on physicochemical characteristics (see discussion below).

Overall assessment factor (AF): 37.5

Dose descriptor: LOAEC

AF for dose response relationship: 3

Justification: LOAEL/NAEL extrapolation

AF for differences in duration of exposure: 1
AF for interspecies differences (allometric scaling): 1
AF for other interspecies differences: 1

Justification: Local effect in the respiratory tract

AF for intraspecies differences: 5

Justification: Worker

AF for the quality of the whole database: 1

Acute/short term exposure

Hazard assessment conclusion:no hazard identified

DNEL related information

Workers - Hazard via dermal route

Systemic effects

Long term exposure

Hazard assessment conclusion:no hazard identified

Acute/short term exposure

Hazard assessment conclusion:no hazard identified

DNEL related information

Local effects

Long term exposure

Hazard assessment conclusion:low hazard (no threshold derived)

Acute/short term exposure

Hazard assessment conclusion:low hazard (no threshold derived)

Workers - Hazard for the eyes

Local effects

Hazard assessment conclusion: low hazard (no threshold derived)

Additional information - workers

1. Introduction

In this dossier, all the toxicological information on Chlorine dioxide (ClO2) are re-examined and analyzed in order to define a DNEL (s)/DMEL (s) for each human health endpoints if possible. The followed method is that proposed in the guidance for the implementation of Reach (Chapter R.8: Characterisation of dose (concentration)-response for human health, May 2008).

2.5

2. Classification according to the CLP Regulation (1272/2008)

The harmonized classification of ClO2 (as gas) is:

- Fatal if inhaled, Category 2 (H330); however, this is a minimum classification (* mark), and based on data, Category 1 is suitable.
- Corrosive, Skin corr. 1B (H314)

The harmonized classification of CIO2 (as aqueous solutions) is:

- Toxic if swallowed, Category 3 (H301)
- Corrosive, Skin corr. 1B (H314)

However, for the concentration range considered in this registration dossier (i.e. 0.6 to 2%), solutions are not considered as corrosive, but only Irritant to eyes, cat.2 (for 0.6 to 2%), and Skin irritant cat.2 above 1%.

An additional self-classification is proposed:

- Harmful if inhaled (Category 4, H332), applying to solutions containing at least 0.82% chlorine dioxide.

3. Worker-DNELs/DMELs derivation according to the toxicological profile of ClO2

Inhalation and dermal exposure were the most appropriate routes for assessing occupational risk in workers. Effects from exposure of animals to ClO2 are limited to the respiratory system: irritation of the nasal mucosa, bronchopneumonia, lymphocytic infiltration of the alveolar spaces, alveolar vascular congestion, haemorrhagic alveoli, epithelial erosions, and inflammatory infiltrations of the bronchi caused by important local irritation.

Neither indications of systemic toxicity nor evidence of a reprotoxic potential were observed. Tests assessing the mutagenic potential of ClO2 in vivo provided no evidence of any mutagenic or genotoxic activity. Therefore, DNELs were only derived for local effects.

3.1 Worker-DNEL acute - local effects:

3.1.1 Inhalation route:

A key study was identified for this endpoint, LC₅₀inhalation = 89 mg/m3 air (Kr. 1, EU Method B.2, GLP, Schorsch et al., 1996) (see § 7.2.2).

Clinical signs observed in all dose groups included: respiratory distress and general weakness. Lungs from treated animals showed frequent mottling, redness and depressed area. The main lesion induced by ClO2 is the destruction of alveolar walls, which creates pulmonary emphysema lesions. This emphysema was found on all rats of the study (except control)

whatever the tested concentration. The severity of the lesion is proportional to the dose. Animals died by respiratory deficiency showing that the mechanism of action is corrosivity.

This study classifies ClO2 as Fatal if inhaled (Category 1 H330). but Category 4 for the concentration range considered (0.6% to 2%). Therefore, a qualitative risk assessment shall be considered, since high toxicity is sufficient to warrant a strict control of potential exposure (see R.8, Box 8, p113). The RMMs/OCs should ensure that peak concentrations exceeding the long-term DNEL will not occur.

3.1.2 Dermal route:

No acute toxicity study by dermal route was available. Since ClO2 is classified as corrosive again not for the concentration range considered, maximum EDI2 +SCI2, and since no systemic effects were expected no test was proposed considering animal welfare. Hence only qualitative assessment can be performed following the approach described in the dossier to define the risk management measures (RMMs) and operational conditions (OCs).

- 3.2 Worker-DNEL long-term local effects:
- 3.2.1 Inhalation route:

Introduction

The threshold limit value TLV-TWA: 0.28 mg/m3 (0.1 ppm) is recommended by the Conference of Governmental Industrial Hygienists (ACGIH, 2001). This value was set based on:

- the repeated dose toxicity study by inhalation of Dahlamn (1957) identifying a NOEC of 0.28 mg/m3 in rats exposed 5h/day for 10 weeks to chlorine dioxide gas.
- the clinical investigation conducted on workers by Gloemme and Lundgren (1957) attributing effects to short periods of exposure at concentrations considerably in excess of 0.28 mg/m3 of ClO2 and chlorine gas.

The value of 0.28 mg/m3 is used without the application of any assessment factor for the derivation of the TLV-TWA. However, the clinical investigation of Gloemme and Lundgren (1957) does not properly describe and justify the recruitment procedures of the study workers. The characterization of exposure is not adequate: atmospheric concentrations were not measured continuously. Consideration of bias and confounding factors is not done and statistics could not be done as the worker numbers is too low (only three cases are reported).

In conclusion bias are numerous in this study. Therefore, according to the draft guidance for DNEL derivation from human data (2010) this study considered as inadequate (low quality) is not taken for derivation.

Consequently, the studies conducted by Paulet and Debrousses (1970, 1971) which include more details than those of Dalhamn are used for the DNEL derivation.

DNEL derivation

The concentration descriptor is obtained from the sub-acute inhalation toxicity studies of Paulet and Debrousses (1970, 1971). Collectively these studies suggested that effects from repeated exposure in rats exposed to Chlorine dioxide gas by inhalation are limited to effects on the respiratory tract due to local irritation. A LOAEC of 2.76 mg/m3 was determined for these local effects based on peribronchiolar oedema and vascular congestion in the lungs observed in the two-month study (Paulet and Debrousses, 1971).

To describe the ClO2 uptake in the respiratory tract, the gas categorization scheme of EPA (EPA/600/8-90/066F, October 1994) was used. This scheme separates gases into three categories based on physicochemical characteristics:

- Category 1 gases are defined as highly water soluble and/or irreversibly reactive gases. These gases do not significantly accumulate in the blood.
- Category 2 gases are moderately water soluble and rapidly reversible reactive or moderately to slowly irreversibly metabolized in respiratory tract tissue.
- Category 3 gases are relatively water insoluble and unreactive in the extrathoracic and tracheobronchial regions.

CIO2 is defined as a Category 1 gas as it is water soluble and rapidly reduced in contact with organic compounds. Based on this assumption a regional gas dose ratio (RGDR) of CIO2 can be calculated for extrathoracic (ET), tracheobronchial (TB) and pulmonary (PU) regions using empirical models (see attached document). A human equivalent concentration (HEC) for the LOAEL was thereafter calculated by multiplying the LOAEC and the RGDRs.

The following table indicates the inhalation DNEL-long term for local effect calculation.

Table 1.1: Calculation of long-term DNEL by inhalation for local effects of Chlorine dioxide:

Worker Local long-term DNEL / inhalation

| Step a: Determination of the critical dose | | | |
|----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--|--|
| Key studies | Paulet and Debrousses (1970, 1971), K4, WoE | | |
| Relevant dose descriptor | LOAEC = 2.76 mg/m ³ for local irritant effects | | |
| Step b: Correction for Human Equivalent Concentra | ation | | |
| | RGDR _{ET} = 0.178 | | |
| Regional Gas Dose Ratios (RGDR) | RGDR _{TB} = 1.815 | | |
| | RGDR _{PU} = 2.167 | | |
| Overall RGDR | RGDRs = 4.129 | | |
| Adjusted dose descriptor = relevant dose descriptor x RGDRs | LOAEC _{HEC} = 11.40 mg/m ³ | | |
| Step c: Correction for uncertainty factors | | | |
| Differences in metabolic rate per b.w. (allometric scaling) | (local effects) | | |
| Differences in absorption depending on route of exposure (route-route extrapolation, human/animal) | - (local effects) | | |
| Modification for exposure (experiment and human) | - (local irritant effects depending on concentration only) | | |
| Correct starting point = adjusted dose descriptor / overall factor for uncertainties | 11.4 mg/m ³ | | |
| Step d: Correction for assessment factors | | | |
| Interspecies differences | 2.5 (effects on respiratory tract) | | |
| Intraspecies differences | 5 (worker) | | |
| Duration extrapolation | 1 | | |
| (sub-acute/sub-chronic/chronic) | (similar respiratory irritant effects were observed after acute exposure in rats) | | |
| Issues related to dose-response | 3 (LOAEL/NAEL extrapolation) | | |
| Quality of whole database | 1 | | |
| Overall assessment factor | 37.5 | | |
| DNEL calculation | 0.304 mg/m ³ | | |
| | 0.11 ppm | | |

DNEL ppm= DNEL mg/m3* 24.05 / MW at 20°C = 0.304 * 24.45 / 67.45 at 25°C

Conclusion

The inhalation DNEL long-term for local effects is 0.304 mg/m3in the workers.

3.2.2 Dermal route:

No repeated toxicity study by dermal route was available. Since ClO2 (gas) is classified as corrosive to the skin not for the concentration range considered (0.6% to 2%), maximum EDI2 +SCI2.

and since no systemic effects were expected at non-irritating doses no test was proposed considering animal welfare. Hence only qualitative assessment can be performed following the approach described in the dossier to define the risk management measures (RMMs) and operational conditions (OCs).

General Population - Hazard via inhalation route

Systemic effects

Long term exposure

Hazard assessment conclusion: no hazard identified

Acute/short term exposure

Hazard assessment conclusion: no hazard identified

DNEL related information

Local effects

Long term exposure

Hazard assessment conclusion: no hazard identified

Acute/short term exposure

Hazard assessment conclusion: no hazard identified

DNEL related information

General Population - Hazard via dermal route

Systemic effects

Long term exposure

Hazard assessment conclusion: no hazard identified

Acute/short term exposure

Hazard assessment conclusion: no hazard identified

DNEL related information

Local effects

Long term exposure

Hazard assessment conclusion: no hazard identified

Acute/short term exposure

Hazard assessment conclusion: no hazard identified

General Population - Hazard via oral route

Systemic effects

Long term exposure

Hazard assessment conclusion: no hazard identified

Acute/short term exposure

Hazard assessment conclusion: no hazard identified

DNEL related information

General Population - Hazard for the eyes

Local effects

Hazard assessment conclusion: no hazard identified

Additional information - General Population

Indirect exposure of humans via the environment is very unlikely due to the high reactivity of ClO2 and consumers are not exposed to ClO2. Therefore, no hazard is identified for general population exposure to Chlorine dioxide.

Skin irritation / corrosion

Endpoint conclusion

Endpoint conclusion: adverse effect observed (corrosive)

Eye irritation

Endpoint conclusion

Endpoint conclusion: adverse effect observed (irritating)

Additional information

In accordance with column 2 of REACH Annex VIII, the in vivo skin irritation study (required in section 8.1.1) and the in vivo eye irritation study (required in section 8.2.1) do not need to be conducted as the substance is classified as corrosive to the skin based on the results of the acute oral toxicity study of Tos (1996).

Effects on skin irritation/corrosion: corrosive

Effects on eye irritation: corrosive

Skin sensitisation

Endpoint conclusion: no adverse effect observed (not sensitising)

Repeated dose toxicity: via oral route - systemic effects

Endpoint conclusion

Dose descriptor: NOAEL

11.5 mg/kg bw/day

Study duration: subchronic

Species: rat

Repeated dose toxicity: inhalation - systemic effects

Endpoint conclusion

Dose descriptor: LOAEC

2.8 mg/m³

Study duration: subacute Species: rat

Additional information

Repeated dose toxicity: oral

In a subchronic toxicity study (Daniel et al., 1990) performed similarly to the OECD test guideline No. 408, Chlorine Dioxide (ClO2) was administered in drinking water to rats at dose levels of 0, 25, 50, 100 and 200 mg/L.

There were no deaths recorded at any dose level. No treatment-related changes were noted for haematology and biochemistry parameters.

Changes in the levels of the enzymes, lactate dehydrogenase (LDH) and aspartate aminotransferase (AST) at 100 and 200 mg/L and AST at 25 and 50 mg/L in male animals were noted. There was a significant decreased body weight in both sexes at 200 mg/L. A dose-related decrease in liver weight was observed in both sexes and in spleen weights in females only. However, all these changes may be explicated by a decrease in the water consumption observed in all the treated groups.

Genetic Toxicity

Chlorine dioxide is not classified as genotoxic considering the overall results from the in vivo studies.

Carcinogenicity

Chlorine dioxide should not be considered as a substance with a carcinogenic potential.

Reproductive Toxicity

Under test conditions, there were no adverse effects on reproduction and fertility, therefore:

The NOAEL (Parental) = 88 mg ClO₂/kg bw/d, based on the haemato toxicity observed at 330 mg ClO₂/kg bw/d.

The NOAEL (Developmental) = $330 \text{ mg ClO}_2/\text{kg bw/d}$, the highest dose tested.

The NOAEL (Fertility) = 330 mg ClO_2/kg bw/d, the highest dose tested.

Even if the results of the study showed that parental toxicity is observed at 300 ppm, CIO_2 has corrosive properties at doses as low as 40 mg/kg bw (Tos, 1996) and so effects that will be observed will be linked to corrosive properties rather than to repeated dose toxicity.

Neurotoxicity:

Based on the results of studies, the NOAEL for neurotoxicity is 300 ppm, the highest dose tested corresponding to 330 mg/kg bw/d of ClO₂.

Even if the results of the study showed that ClO_2 is of low level of concern for neurotoxicity at doses above 88 mg/kg bw, it has corrosive properties at doses as low as 40 mg/kg bw (Tos, 1996) and so effects that will be observed will be linked to corrosive properties rather than neurotoxicity.

Information on the likely routes of exposure

Skin and eye contact - YES (Liquid/Vapours/Mist)

Inhalation - YES (Vapours/Mist)

Ingestion - YES (Unhygienic practices)

Symptoms related to the physical, chemical and toxicological characteristics

Data for Chlorine Dioxide

Acute toxicity: oral

A study was identified as the key study (Tos, 1996). The study was conducted according to the OECD guideline No. 401 and in compliance with GLP. Rats were administered Chlorine dioxide (as a 0.2 % solution in water) by gavage at doses of 20, 40 and 80 mg/kg bw.

Animals treated at the lowest dose showed hypoactivity, piloerection and hunched posture during the first three days of the study. Females treated at 40 mg/kg bw showed the same clinical signs up to day 5 of the study. Males treated at 40 mg/kg bw and all animals treated at the highest dose showed clinical signs involving the CNS, the respiratory tract, and also piloerection, hunched posture and salivation. All reviving animals recovered within days 4 - 7 of the study. The autopsy of animals which died during the study showed test substance-related changes in the gastrointestinal tract: congestion and erosions with mucus or test substance presence in the stomach and thinning walls with catarrhal or catarrhal-haemorrhagic content in the intestine. Congestion of the lungs, of the kidneys and of the liver and decreased size of the spleen were also observed. Animals treated at 20 mg/kg bw not show any necroscopic changes at the autopsy performed at the end of the study. The surviving animals treated at the highest doses (40 and 80 mg/kg bw) showed changes in the stomach (thickening of the glandular mucosa) which were considered test substance related. Oral LD₅₀Combined = 93.86 mg/kg bw (95% C.L. of 45.52 - 193.53 mg/kg bw). Observed effects are related to the corrosive properties of ClO₂.

Acute toxicity: dermal

In accordance with REACH requirements, the acute dermal toxicity study (required in section 8.5.3) does not need to be conducted as results for two routes of exposure (oral and inhalation) are already available.

Acute toxicity: inhalation

A study was identified as the key study (Schorsch et al., 1996). The study was conducted according to the EU Method B.2 and in compliance with GLP. Rats were exposed by oro-nasal inhalation to Chlorine Dioxide gas for 4 hours at analytical concentrations of 0, 46, 71, 107 and 128 mg/m 3 . Clinical signs observed in all dose groups included: respiratory distress (abdominal respiration, noisy respiration, laboured respiration and nasal secretion) and general weakness (piloerection, hunched back, decrease of activity and weight loss / thin body condition). Lungs from treated animals showed frequent mottling, redness and depressed area. The main lesion induced by ClO_2 is the destruction of alveolar walls, which created dose-related pulmonary emphysema lesions. Inhalation LC_{50} combined = 89 mg/m 3 air (95% CL 69 -119 mg/m 3).

In a key study performed in accordance with GLP and OECD Guideline 403, groups of CD / Crl:CD(SD) rats were exposed to 0.6% aqueous chlorine dioxide (ClO2) solution, inherently stabilized *, at actual concentrations of 0.030, 0.047 and 0.074 mg/L air for 4 h by inhalation (mist) using a dynamic nose-only exposure chamber. The exposure concentrations were determined by iodometry. Animals were then observed for mortality, clinical signs and bodyweights for 14 days and necropsy was performed in all animals for macroscopical examination.

In the inhalation chamber, close to the animals' noses, the spray-jet generated atmosphere had mass median aerodynamic diameters (MMAD) between 2.388 and 2.467 μ m as determined with a cascade impactor. The Geometric Standard Deviations (GSD) of the MMAD were calculated as 2.69, 2.74 and 2.78.

At the concentration of 0.074 mg/L air, slight ataxia, slight tremor and slight to moderate dyspnoea and premature death in all 3/3 male and 3/3 female animals. At the concentration of 0.047 mg/L air, slight ataxia, slight tremor and slight dyspnoea in all 5/5 male and 5/5 female animals. Two of 5 male and 2 of 5 female animals died prematurely. At the concentration of 0.030 mg/L air, slight ataxia, slight tremor and slight dyspnoea in all 5/5 male and 5/5 female animals. None of 5 male and 1/5 female animals died prematurely. All surviving animals gained the expected body weight. No pathological findings were noted at necropsy.

LC₅₀ for males and females were 0.048 and 0.040 mg/L air/4 h, respectively.

 LC_{50} males and females combined (14 days): 0.041 mg/L air/4 h as pure ClO_2 . Therefore, the LC_{50} value corresponds to 6.83 mg 0.6% ClO_2 solution/L air/4h which is lower to the classification limit for a mist according to the CLP.

According to the study results, and applying the criteria for classification for acute inhalation toxicity (mist/aerosol), chlorine dioxide solutions have to be classified as category 4 for acute inhalation toxicity (ATI4) with a specific concentration limit (i.e. threshold concentration, below which no classification of the solution is warranted) of 0.82%, based on prorata of concentration according to CLP Regulation.

Justification for selection of acute toxicity – oral endpoint Key study conducted on 0.2% chlorine dioxide aqueous solution (OECD 401, K, rel.1).

Justification for selection of acute toxicity – inhalation endpoint Key study conducted on 0.6% chlorine dioxide solution (OECD 402, K, rel.2).

Justification for selection of acute toxicity – dermal endpoint

In accordance with REACH requirements, the acute dermal toxicity study (required in section 8.5.3) does not need to be conducted as results for two routes of exposure (oral and inhalation) are already available.

Delayed and immediate effects and also chronic effects from short and long term exposure

Skin corrosion/irritation:

Irritant to skin and mucous membranes.

Serious eye damage/irritation:

Strong irritant with the danger of severe eye injury.

Respiratory or skin sensitisation:

No sensitising effects known.

Numerical measures of toxicity (such as acute toxicity estimates)

Acute toxicity: via oral route

Endpoint conclusion: adverse effect observed

Dose descriptor: LD₅₀ 94 mg/kg bw

Acute toxicity: via inhalation route

Endpoint conclusion: no adverse effect observed

Dose descriptor: LC₅₀ 6 830 mg/m³

Acute toxicity: via dermal route

Endpoint conclusion: no study available

Interactive effects

None known.

Where specific chemical data are not available

None known.

Mixtures

No data available.

Mixture versus ingredient information

Not available.

Other information

None.

12 Ecological information

Toxicity

Data for Chlorine Dioxide

Freshwater

Hazard assessment conclusion: PNEC aqua (freshwater)

PNEC value: $0.021 \,\mu\text{g/L}$ Assessment factor: $1 \, 000$

Extrapolation method: assessment factor

PNEC freshwater (intermittent releases): 0.2 μg/L

Marine water

Hazard assessment conclusion: PNEC aqua (marine water)

PNEC value: 0.021 µg/L

Assessment factor: 1 000

Extrapolation method: assessment factor

STP

Hazard assessment conclusion:

PNEC STP
PNEC value:

0.01 mg/L
Assessment factor:

1 000

Extrapolation method: assessment factor

Sediment (freshwater)

Hazard assessment conclusion: no data available: testing technically not feasible

Sediment (marine water)

Hazard assessment conclusion: no data available: testing technically not feasible

Hazard for air

No data

Hazard for terrestrial organisms

Soil

Hazard assessment conclusion: no data available: testing technically not feasible

Hazard for predators

Secondary poisoning

Hazard assessment conclusion: no potential for bioaccumulation

Persistence and degradability

No tests currently exists to test persistence and degradability for mixtures.

Bioaccumulative potential

No potential for bioaccumulation.

Mobility in soil

No tests currently exists to test mobility in soil for mixtures.

Other adverse effects

None known.

13 Disposal considerations

Disposal methods

Waste disposal recommendations:

Dispose of waste and container 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. Recycle/reuse. Remove for physico-chemical/biological treatment. **DO NOT** discharge into drains or the environment.

Ecology - waste materials:

DO NOT release to the environment.

Empty Container:

DO NOT reuse container. Rinse thoroughly before discarding in chemical waste or return to supplier.

14 Transport information

UN Number

UN1760 Class 8 PG III Exempt 200 F: 5

UN Proper Shipping Name

CORROSIVE LIQUID, N.O.S.

Transport hazard class(es)

8



Packing group, if applicable

III Exempt Quantity: 200Kg

Environmental hazards

Acute toxicity to aquatic life. Category: 2

Special precautions for user

DO NOT load with Classes 1 and 2.3.

Cyanides **must not** be transported with acid.

May be loaded with Classes 2.1, 2.2, 5.2, 6.1 and 6.2 if kept at least 1 metre apart.

Concentrated acids and bases must be kept at least 1 metre apart.

Can be loaded with all other classes.

Goods of different classes **must** be segregated by an air space of at least 100mm or by an approved segregation device or non-dangerous goods.

P, B, L and O provisions as per SANS 10231:2006

B9b Carriage in bulk is permitted, as a full load, in sheeted vehicles, in closed containers or in sheeted containers with complete walls. For substances of class 8, the body of the vehicle or container shall be equipped with a suitable and sufficiently stout inner lining.

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code

Not applicable.

15 Regulatory information

Safety, health and environmental regulations specific for the product in question

SA NATIONAL LEGISLATION

Hazardous Substances Act 15 of 1973 and Regulations.

Occupational Health and Safety Act 85 of 1993 and Regulations.

SA NATIONAL STANDARDS

SANS 10228: 2006: Identification and Classification of Dangerous Goods for Transport by Road and Rail.

SANS 10231 : 2018 : Transport of dangerous goods - Operational requirements for road vehicles. SANS 10234 : 2008 : Globally Harmonized System of classification and labelling of chemicals (GHS).

SANS 11014: 2010: Safety Data Sheets for chemical Products.

REACH Regulation (EC) No 1907/2006

This product contains only components that have been either pre-registered, registered, are exempt from registration, are regarded as registered or are not subject to registration according to Regulation (EC) No. 1907/2006 (REACH)., The aforementioned indications of the REACH registration status are provided in good faith and believed to be accurate as of the effective date shown above. However, no warranty, express or implied, is given. It is the buyer's/user's responsibility to ensure that his/her understanding of the regulatory status of this product is correct.

Seveso III: Directive 2012/18/EU

Listed in Regulation: Not applicable

US Federal Regulations

EPA FIFRA Information

This chemical is a pesticide product registered by the Environmental Protection Agency (EPA Registration Number 75757-

2-80802) and is subject to certain labeling requirements under federal pesticide law. These requirements differ from the classification criteria and hazard information required for safety data sheets, and for workplace labels of non-pesticide chemicals. Following is the hazard information as required on the pesticide label:

CAUTION Causes moderate eye irritation. Avoid contact with eyes, skin, or clothing. Harmful if swallowed, absorbed through the skin, or inhaled. Wash thoroughly with soap and water after handling, and before eating, drinking, chewing gum, using tobacco, or using the toilet.

TSCA (Toxic Substances Control Act) Status - United States

The intentional ingredients of this material are listed.

CERCLA RQ-40 CFR 302.4(a)

None listed

SARA 302 Components - 40 CFR 355 Appendix A

None

SARA 313 Components - 40 CFR 372.65

Section 313 Components CAS Number Percent (%)

Chlorine dioxide 10049-04-4 0.3 (Note: the concentration is below the 1.0% de minimis value)

OSHA Process Safety Management 29 CFR 1910

PSM Component(s) Condition TQ (lbs)
CHLORINE DIOXIDE 1000

EPA Accidental Release Prevention 40 CFR 68

PSM Component(s) Condition TQ (lbs)
CHLORINE DIOXIDE 1000

Chlorine Oxide (ClO2)

International Regulations

Not determined

US State and Local Regulations

California Proposition 65:

None on list.

Chemical safety assessment:

No assessment was compiled for this product.

16 Other information

Other information

Full text of H-Statements referred to under section 2

Hazard statements

H315 Causes skin irritation.

H319 Causes serious eye irritation.

H332 Harmful if inhaled. H401 Toxic to aquatic life.

Precautionary statements

P264 Wash thoroughly after handling.

P271 Use only outdoors or in a well-ventilated area.

P280 Wear protective gloves/protective clothing/eye protection/face protection.

P302+P352 IF ON SKIN: Wash with plenty of soap and water.

P304+P340 IF INHALED: Remove victim to fresh air and Keep at rest in a position comfortable for breathing.
P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and

easy to do. Continue rinsing.

P332+P313 If skin irritation occurs: Get medical advice/attention.
P337+P313 IF eye irritation persists: Get medical advice/attention.
P362+P364 Take off contaminated clothing and wash it before reuse.

P370+P378 In case of fire: Use water to extinguish.

P405 Store locked up.

P501 Dispose of contents and container in accordance with local, regional, national, international

regulations.

Labelling REGULATION (EC) No 1272/2008

Signal Word

Warning

Pictograms Hazard to Human

GHS07 Health Hazard

Pictogram Hazard during Transport

Class 8 Corrosive

Training advice

Provide adequate information, instruction and training for operators.

Compiled by Aquatrade Water Treatment Chemicals (Pty) Ltd, R. van Rooyen, SHEQ Co-ordinator and E. Le Sar, Director.

MANUFACTURER/SUPPLIER DISCLAIMER:

IMPORTANT: This information is given without a warranty or guarantee. No suggestions for use are intended or shall be construed as a recommendation to infringe any existing patents or violate any national or local laws. Safe handling and use is the responsibility of the customer. Read the label before using this product. This information is true and accurate to the best of our knowledge.

Revision History

| Revision: | Date: | Change: |
|-----------|------------|----------------------------------------------------------------------|
| | | Preparation of the safety data sheet according to Regulation (EC) No |
| 1.0 | 2018/04/16 | 1907/2006 of the European Parliament and of the Council |
| 2.0 | 2019/03/08 | Section 2 to 14. Reclassification of product |
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