

## manganese dioxide

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

#### 1.1. Product identifier

<b>Product name</b>	: manganese dioxide
<b>Synonyms</b>	: MnO <sub>2</sub> rich material, cell mud, anode mud, MnO <sub>2</sub> sludge, Pb Mn cell mud, manganese sludge, anode cleaning sludge; slimes and sludges, zinc sulfate electrolytic
<b>Registration number REACH</b>	: 01-2119467168-30-0000 (Nyrstar Belgium NV/SA) 01-2119467168-30-0003 (Nyrstar Budel BV) 01-2119467168-30-0006 (Nyrstar France SAS)
<b>Product type REACH</b>	: Transported isolated intermediate : On-site isolated intermediate
<b>CAS number</b>	: 69012-43-7
<b>EC number</b>	: 273-742-8

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

##### 1.2.1 Relevant identified uses

Under Regulation (EC) No 1907/2006 the substance is defined as an on-site and transported isolated intermediate and must be used in correspondence to that status, including the application of strictly controlled conditions

Industrial use: manufacturing of chemicals

For further details concerning the management measures: see the 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.  
Zinkstraat 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  
☎ +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 Aubry  
☎ +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

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
Carc.	category 2	H351: Suspected of causing cancer.
Repr.	category 1A	H360: May damage fertility or the unborn child.
STOT RE	category 1	H372: Causes damage to organs (central nervous system, reproductive organs) through prolonged or repeated exposure if swallowed.
Acute Tox.	category 4	H332: Harmful if inhaled.
Acute Tox.	category 4	H302: Harmful if swallowed.

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Aquatic Acute	category 1	H400: Very toxic to aquatic life.
Aquatic Chronic	category 1	H410: Very toxic to aquatic life with long lasting effects.

## 2.2. Label elements



**Signal word**



Danger



### H-statements

H351	Suspected of causing cancer.
H360	May damage fertility or the unborn child.
H372	Causes damage to organs (central nervous system, reproductive organs) through prolonged or repeated exposure if swallowed.
H302 + H332	Harmful if swallowed or if inhaled.
H410	Very toxic to aquatic life with long lasting effects.

### P-statements

P280	Wear protective gloves, protective clothing and eye protection/face protection.
P260	Do not breathe dust.
P304 + P340	IF INHALED: Remove person to fresh air and keep comfortable for breathing.
P330	Rinse mouth.
P308 + P313	IF exposed or concerned: Get medical advice/attention.
P312	Call a POISON CENTER/doctor if you feel unwell.

### Supplemental information

Restricted to professional users.

## 2.3. Other hazards

No other hazards known

## SECTION 3: Composition/information on ingredients

### 3.1. Substances

Name REACH Registration No	CAS No EC No	Conc. (C)	Classification according to CLP	Note	Remark	M-factors and ATE
zinc oxide	1314-13-2 215-222-5	0%<C<1%	Aquatic Acute 1; H400 Aquatic Chronic 1; H410	(1)(2)	Component	M: 1 (Acute, ECHA) M: 1 (Chronic, ECHA)
lead(II)sulphate	7446-14-2 231-198-9	2.93% <C<29.27%	Repr. 1A; H360Df Acute Tox. 4; H332 Acute Tox. 4; H302 STOT RE 2; H373 Aquatic Acute 1; H400 Aquatic Chronic 1; H410 Repr. 2; H361f: C≥2,5%, (CLP Annex VI (ATP 0)) STOT RE 2; H373: C≥0,5%, (CLP Annex VI (ATP 0))	(1)(2)(10)	Component	M: 1 (Acute, BIG)
manganese dioxide	1313-13-9 215-202-6	55.36% <C<94.91%	Acute Tox. 4; H332 Acute Tox. 4; H302 STOT RE 2; H373	(1)(2)(6)	Component	
calcium sulfate	7778-18-9 231-900-3	0% <C<4.85%		(2)	Component	
strontium sulphate	7759-02-6 231-850-2	0% <C<5.24%			Component	

- (1) For H- and EUH-statements in full: see section 16  
 (2) Substance with a Community workplace exposure limit  
 (6) Enumerated in Annex VI of Regulation (EC) No. 1272/2008 but the classification has been adapted after evaluation of available test data  
 (10) Subject to restrictions of Annex XVII of Regulation (EC) No. 1907/2006

### 3.2. Mixtures

Not applicable

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## SECTION 4: First aid measures

### 4.1. Description of first aid measures

#### General:

Check the vital functions. Unconscious: maintain adequate airway and respiration. Respiratory arrest: artificial respiration or oxygen. Cardiac arrest: perform resuscitation. Victim conscious with laboured breathing: half-seated. Victim in shock: on his back with legs slightly raised. Vomiting: prevent asphyxia/aspiration pneumonia. Prevent cooling by covering the victim (no warming up). Keep watching the victim. Give psychological aid. Keep the victim calm, avoid physical strain. Depending on the victim's condition: doctor/hospital.

#### After inhalation:

Remove the victim into fresh air. Respiratory problems: consult a doctor/medical service.

#### After skin contact:

Rinse with water. Soap may be used. Take victim to a doctor if irritation persists.

#### After eye contact:

Rinse with water. Remove contact lenses, if present and easy to do. Continue rinsing. Take victim to an ophthalmologist if irritation persists.

#### After ingestion:

Rinse mouth with water. Immediately after ingestion: give lots of water to drink. Do not induce vomiting. Consult a doctor/medical service if you feel unwell.

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

#### 4.2.1 Acute symptoms

##### After inhalation:

No effects known.

##### After skin contact:

No effects known.

##### After eye contact:

No effects known.

##### After ingestion:

Vomiting. Abdominal pain. Diarrhoea. Irritation of the gastric/intestinal mucosa.

#### 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

The information in this section is a general description. If available, the documentation for isolated intermediates will be attached in annex to support safe handling arrangements.

### 5.1. Extinguishing media

#### 5.1.1 Suitable extinguishing media:

Adapt extinguishing media to the environment for surrounding fires.

#### 5.1.2 Unsuitable extinguishing media:

Not applicable.

### 5.2. Special hazards arising from the substance or mixture

On burning: release of harmful/irritant gases/vapours.

### 5.3. Advice for firefighters

#### 5.3.1 Instructions:

Take account of environmentally hazardous firefighting water. Use water moderately and if possible collect or contain it.

#### 5.3.2 Special protective equipment for fire-fighters:

Gloves (EN 374). Safety glasses (EN 166). Protective clothing (EN 14605 or EN 13034). Reactivity hazard: self-contained breathing apparatus (EN 136 + EN 137). Reactivity hazard: gas-tight suit (EN 943). Dust cloud production: self-contained breathing apparatus (EN 136 + EN 137). Heat/fire exposure: self-contained breathing apparatus (EN 136 + EN 137).

## SECTION 6: Accidental release measures

The information in this section is a general description. If available, the documentation for isolated intermediates will be attached in annex to support safe handling arrangements.

### 6.1. Personal precautions, protective equipment and emergency procedures

Prevent dust cloud formation. No naked flames.

#### 6.1.1 Protective equipment for non-emergency personnel

See section 8.2

#### 6.1.2 Protective equipment for emergency responders

Gloves (EN 374). Safety glasses (EN 166). Protective clothing (EN 14605 or EN 13034). Reactivity hazard: self-contained breathing apparatus (EN 136 + EN 137). Reactivity hazard: gas-tight suit (EN 943). Dust cloud production: self-contained breathing apparatus (EN 136 + EN 137).

#### 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 solid spill. Knock down/dilute dust cloud with water spray. Take account of toxic/corrosive precipitation water. Prevent soil and water pollution. Prevent spreading in sewers.

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## 6.3. Methods and material for containment and cleaning up

Prevent dust cloud formation. Scoop solid spill into closing containers. Carefully collect the spill/leftovers. 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.

## SECTION 7: Handling and storage

The information in this section is a general description. If available, the documentation for isolated intermediates will be attached in annex to support safe handling arrangements.

### 7.1. Precautions for safe handling

Avoid raising dust. Keep away from naked flames/heat. Observe very strict hygiene - avoid contact. Remove contaminated clothing immediately. Do not discharge the waste into the drain. 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 only in the original container. Store at ambient temperature. Meet the legal requirements.

#### 7.2.2 Keep away from:

Heat sources, combustible materials, oxidizing agents, reducing agents, (strong) acids, organic materials.

#### 7.2.3 Suitable packaging material:

No data available

#### 7.2.4 Non suitable packaging material:

No data available

### 7.3. Specific end use(s)

If available, the documentation for isolated intermediates will be attached in annex to support safe handling arrangements.

## SECTION 8: Exposure controls/personal protection

### 8.1. Control parameters

#### 8.1.1 Occupational exposure

##### a) Occupational exposure limit values

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

#### EU

Inorganic lead and its compounds	Time-weighted average exposure limit 8 h (Binding occupational exposure limit value)	0.15 mg/m <sup>3</sup>
Manganese and inorganic manganese compounds (as manganese)	Time-weighted average exposure limit 8 h (Indicative occupational exposure limit value)	0.05 mg/m <sup>3</sup> (2)
	Time-weighted average exposure limit 8 h (Indicative occupational exposure limit value)	0.2 mg/m <sup>3</sup> (1)

(2): Respirable fraction

(1): Inhalable fraction

#### Belgium

Calcium (sulfate de) (anhydrate, hemihydrate, dihydrate, gypse)	Time-weighted average exposure limit 8 h	10 mg/m <sup>3</sup>
Manganèse et ses composés (en Mn) (fraction respirable)	Time-weighted average exposure limit 8 h	0.2 mg/m <sup>3</sup>
Plomb inorg. (poussières et fumées) (en Pb)	Time-weighted average exposure limit 8 h	0.15 mg/m <sup>3</sup>
Zinc (oxyde de) (fraction alvéolaire)	Time-weighted average exposure limit 8 h	2 mg/m <sup>3</sup>
	Short time value	10 mg/m <sup>3</sup>

#### The Netherlands

Lood en anorganische loodverbindingen	Time-weighted average exposure limit 8 h (Public occupational exposure limit value)	0.15 mg/m <sup>3</sup>
Mangaan en anorganische mangaan-verbindingen (als mangaan)	Time-weighted average exposure limit 8 h (Public occupational exposure limit value)	0.05 mg/m <sup>3</sup>
	Time-weighted average exposure limit 8 h (Public occupational exposure limit value)	0.2 mg/m <sup>3</sup>

#### France

Calcium (sulfate de)	Time-weighted average exposure limit 8 h (VL: Valeur non réglementaire indicative)	10 mg/m <sup>3</sup>
Manganèse et ses composés fraction alvéolaire exprimé en manganèse	Time-weighted average exposure limit 8 h (VRI: Valeur réglementaire indicative)	0.05 mg/m <sup>3</sup>
Manganèse et ses composés fraction inhalable exprimé en manganèse	Time-weighted average exposure limit 8 h (VRI: Valeur réglementaire indicative)	0.20 mg/m <sup>3</sup>
Plomb métallique et composés, en Pb	Time-weighted average exposure limit 8 h (VRC: Valeur réglementaire contraignante)	0.1 mg/m <sup>3</sup>

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Zinc (oxyde de, fumées)	Time-weighted average exposure limit 8 h (VL: Valeur non réglementaire indicative)	5 mg/m <sup>3</sup>
Zinc (oxyde de, poussières)	Time-weighted average exposure limit 8 h (VL: Valeur non réglementaire indicative)	10 mg/m <sup>3</sup>

## Germany

Blei und anorganischen Bleiverbindungen	Time-weighted average exposure limit 8 h (TRGS 505)	0.1 mg/m <sup>3</sup>
Calciumsulfat	Time-weighted average exposure limit 8 h (TRGS 900)	6 mg/m <sup>3</sup>
Mangan und seine anorganischen Verbindungen	Time-weighted average exposure limit 8 h (TRGS 900)	0.02 mg/m <sup>3</sup>
	Time-weighted average exposure limit 8 h (TRGS 900)	0.2 mg/m <sup>3</sup>

## Austria

Calciumsulfat	Tagesmittelwert (MAK)	5 mg/m <sup>3</sup>
	Kurzzeitwert 60(Miw) 2x (MAK)	10 mg/m <sup>3</sup>

## UK

Lead other than lead alkyls	Time-weighted average exposure limit 8 h (Occupational exposure limit (Control of lead at work))	0.15 mg/m <sup>3</sup>
Manganese and its inorganic compounds (as Mn) (Inhalable fraction)	Time-weighted average exposure limit 8 h (Workplace exposure limit (EH40/2005))	0.2 mg/m <sup>3</sup>
Manganese and its inorganic compounds (as Mn) (Respirable fraction)	Time-weighted average exposure limit 8 h (Workplace exposure limit (EH40/2005))	0.05 mg/m <sup>3</sup>

## USA (TLV-ACGIH)

Calcium sulfate	Time-weighted average exposure limit 8 h (TLV - Adopted Value)	10 mg/m <sup>3</sup> (I)
Lead and inorganic compounds, as Pb	Time-weighted average exposure limit 8 h (TLV - Adopted Value)	0.05 mg/m <sup>3</sup>
Manganese, elemental and inorganic compounds, as Mn	Time-weighted average exposure limit 8 h (TLV - Adopted Value)	0.02 mg/m <sup>3</sup> (R)
	Time-weighted average exposure limit 8 h (TLV - Adopted Value)	0.1 mg/m <sup>3</sup> (I)
Zinc oxide	Time-weighted average exposure limit 8 h (TLV - Adopted Value)	2 mg/m <sup>3</sup> (R)
	Short time value (TLV - Adopted Value)	10 mg/m <sup>3</sup> (R)

(I): Inhalable fraction  
(R): Respirable fraction

## b) National biological limit values

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

### Belgium

Plomb et ses composés ioniques (Lood)	sang	70 µg/100ml	
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### USA (BEI-ACGIH)

Lead and inorganic compounds (Lead)	Blood: not critical	200 µg/L	Persons applying this BEI® are encouraged to counsel female workers of child-bearing age about the risk of delivering a child with a PbB over the current CDC reference value.
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## 8.1.2 Sampling methods

Product name	Test	Number
Lead	OSHA	ID 121
Lead	OSHA	ID 125G
Sulfites, & Sulfates	NIOSH	6004
Zinc (Elements)	NIOSH	7300
Zinc (Zn)	NIOSH	7302
Zinc (Zn)	NIOSH	7304
Zinc Oxide	NIOSH	7030
Zinc Oxide	NIOSH	7502
Zinc Oxide	OSHA	ID 121
Zinc Oxide	OSHA	ID 143

## 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

### DNEL/DMEL - Workers

#### zinc oxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	5 mg/m <sup>3</sup>	
	Long-term local effects inhalation	0.5 mg/m <sup>3</sup>	
	Long-term systemic effects dermal	83 mg/kg bw/day	

#### manganese dioxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	0.06 mg/m <sup>3</sup>	
	Long-term systemic effects dermal	0.004 mg/kg bw/day	

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## calcium sulfate

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	21.17 mg/m <sup>3</sup>	
	Acute systemic effects inhalation	5082 mg/m <sup>3</sup>	

## DNEL/DMEL - General population

### zinc oxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	2.5 mg/m <sup>3</sup>	
	Long-term systemic effects dermal	83 mg/kg bw/day	
	Long-term systemic effects oral	0.83 mg/kg bw/day	

### manganese dioxide

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	0.043 mg/m <sup>3</sup>	
	Long-term systemic effects dermal	0.002 mg/kg bw/day	

## calcium sulfate

Effect level (DNEL/DMEL)	Type	Value	Remark
DNEL	Long-term systemic effects inhalation	5.29 mg/m <sup>3</sup>	
	Acute systemic effects inhalation	3811 mg/m <sup>3</sup>	
	Long-term systemic effects oral	1.52 mg/kg bw/day	
	Acute systemic effects oral	11.4 mg/kg bw/day	

## PNEC

### zinc oxide

Compartments	Value	Remark
Fresh water	20.6 µg/l	
Marine water	6.1 µg/l	
STP	100 µg/l	
Fresh water sediment	117.8 mg/kg sediment dw	
Marine water sediment	56.5 mg/kg sediment dw	
Soil	35.6 mg/kg soil dw	

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Compartments	Value	Remark
Fresh water	< 0.01 mg/l	
Marine water	< 0.01 mg/l	
Aqua (intermittent releases)	0.001 mg/l	
STP	100 mg/l	
Fresh water sediment	0.037 mg/kg sediment dw	
Marine water sediment	0.004 mg/kg sediment dw	
Soil	0.028 mg/kg soil dw	

## calcium sulfate

Compartments	Value	Remark
STP	100 mg/l	

### 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 available, the documentation for isolated intermediates will be attached in annex to support safe handling arrangements.

### 8.2.1 Appropriate engineering controls

Avoid raising dust. 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:

Dust production: dust mask with filter type P3. High dust production: self-contained breathing apparatus (EN 136 + EN 137).

#### b) Hand protection:

Gloves.

Materials	Remark
butyl rubber	Good resistance
chlorinated polyethylene	Good resistance
nitrile rubber	Good resistance
neoprene	Good resistance
PVC	Good resistance
chlorinated polyethylene	Good resistance

#### c) Eye protection:

Safety glasses (EN 166). In case of dust production: protective goggles (EN 166).

#### d) Skin protection:

Protective clothing (EN 14605 or EN 13034). Dustproof clothing (EN 13982).

### 8.2.3 Environmental exposure controls:

See sections 6.2, 6.3 and 13

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## SECTION 9: Physical and chemical properties

### 9.1. Information on basic physical and chemical properties

Physical form	Solid
Odour	Odourless
Odour threshold	Not applicable
Colour	Grey to brown-black
Particle size	D50 ; 929 µm D80 ; 2083 µm
Explosion limits	No data available
Flammability	Not classified as flammable
Log Kow	Not applicable
Dynamic viscosity	No data available
Kinematic viscosity	No data available
Melting point	193 °C ; 1013 hPa ; EU Method A.1
Boiling point	No data available
Relative vapour density	Not applicable
Vapour pressure	Not applicable
Solubility	Water ; 28 mg/l ; 20 °C ; OECD 105
Relative density	4.1 ; 22 °C ; EU Method A.3
Absolute density	4090 kg/m <sup>3</sup> ; 22 °C
Decomposition temperature	193 °C ; EU Method A.1 ; 1013 hPa
Auto-ignition temperature	Not applicable
Flash point	Not applicable
pH	2.28 - 2.32 ; 28 mg/l ; 20 °C ; OECD 105

### 9.2. Other information

No data available

## SECTION 10: Stability and reactivity

### 10.1. Reactivity

No data available.

### 10.2. Chemical stability

Stable under normal conditions.

### 10.3. Possibility of hazardous reactions

Reacts with many compounds: (increased) risk of fire/explosion. Reacts with (some) acids: release of toxic and corrosive gases/vapours.

### 10.4. Conditions to avoid

#### Precautionary measures

Avoid raising dust. Keep away from naked flames/heat.

### 10.5. Incompatible materials

Combustible materials, oxidizing agents, reducing agents, (strong) acids, organic materials.

### 10.6. Hazardous decomposition products

No data available.

## SECTION 11: Toxicological information

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

#### 11.1.1 Test results

#### Acute toxicity

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No (test) data available

zinc oxide

Route of exposure	Parameter	Method	Value	Exposure time	Species	Value determination	Remark
Oral	LD50	Equivalent to OECD 401	> 5000 mg/kg		Rat (male / female)	Experimental value	
Dermal	LD50	OECD 402	> 2000 mg/kg bw	24 h	Rat (male / female)	Experimental value	
Inhalation (dust)	LC50	Equivalent to OECD 403	> 5.7 mg/l	4 h	Rat (male / female)	Experimental value	

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## lead(II)sulphate

Route of exposure	Parameter	Method	Value	Exposure time	Species	Value determination	Remark
Oral			category 4			Annex VI	
Inhalation			category 4			Annex VI	

## manganese dioxide

Route of exposure	Parameter	Method	Value	Exposure time	Species	Value determination	Remark
Oral (drinking water)	LD50		> 3480 mg/kg bw		Rat (male)	Experimental value	
Oral			category 4			Annex VI	
Dermal						Data waiving	
Inhalation			category 4			Annex VI	

## calcium sulfate

Route of exposure	Parameter	Method	Value	Exposure time	Species	Value determination	Remark
Oral	LD50	OECD 420	> 1581 mg/kg bw		Rat (female)	Experimental value	
Dermal						Data waiving	
Inhalation (dust)	LC50	OECD 403	> 2.61 mg/l air	4 h	Rat (male / female)	Experimental value	

### **Conclusion**

Harmful if swallowed.

Harmful if inhaled.

Not classified as acute toxic in contact with skin

### **Corrosion/irritation**

#### manganese dioxide

No (test)data available

#### zinc oxide

Route of exposure	Result	Method	Exposure time	Time point	Species	Value determination	Remark
Eye	Not irritating	OECD 405	24 h	24; 72 hours	Rabbit	Experimental value	
Skin	Not irritating	OECD 404	24 h	24 hours	Rabbit	Experimental value	
Not applicable (in vitro test)	Not corrosive	OECD 431	3 minutes	24; 72 hours	Reconstructed human epidermis	Experimental value	

#### manganese dioxide

Route of exposure	Result	Method	Exposure time	Time point	Species	Value determination	Remark
Eye	Slightly irritating	OECD 405		24; 48; 72 hours	Rat	Experimental value	
Skin	Not irritating	OECD 404	4 h	24; 48; 72 hours	Rat	Experimental value	

#### calcium sulfate

Route of exposure	Result	Method	Exposure time	Time point	Species	Value determination	Remark
Eye	Not irritating	OECD 405		24; 48; 72 hours	Rabbit	Experimental value	Single treatment
Skin	Not irritating	OECD 404	4 h	24; 48; 72 hours	Rabbit	Experimental value	

### **Conclusion**

Not classified as irritating to the skin

Not classified as irritating to the eyes

Not classified as irritating to the respiratory system

### **Respiratory or skin sensitisation**

#### manganese dioxide

No (test)data available

#### zinc oxide

Route of exposure	Result	Method	Exposure time	Observation time point	Species	Value determination	Remark
Skin	Not sensitizing	OECD 406			Guinea pig (female)	Experimental value	
Skin	Not sensitizing	Human observation	2 days (continuous)	72 hours	Human	Experimental value	

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Route of exposure	Result	Method	Exposure time	Observation time point	Species	Value determination	Remark
Skin	Not sensitizing	OECD 429			Mouse (female)	Experimental value	

## calcium sulfate

Route of exposure	Result	Method	Exposure time	Observation time point	Species	Value determination	Remark
Skin	Not sensitizing	OECD 406			Guinea pig (male)	Experimental value	

### **Conclusion**

Not classified as sensitizing for skin

Not classified as sensitizing for inhalation

### **Specific target organ toxicity**

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No (test)data available

## zinc oxide

Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Value determination
Oral (diet)	NOEL	OECD 408	3000 ppm		No effect	13 weeks (daily)	Rat (male / female)	Read-across
Dermal	LOAEL	OECD 410	75 mg/kg bw/day		Systemic effects	4 weeks (6h / day, 5 days / week)	Rat (male / female)	Experimental value
Inhalation (aerosol)	NOAEL	OECD 413	1.5 mg/m <sup>3</sup> air		No effect	13 weeks (6h / day, 5 days / week)	Rat (male)	Experimental value

## lead(II)sulphate

Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Value determination
Unknown			STOT RE cat.2					Annex VI
Oral (diet)	Dose level		500 ppm	Blood	Change in the haemogramme/blood composition	7 weeks (daily)	Bovine (male)	Experimental value

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Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Value determination
Oral								Data waiving
Dermal								Data waiving
Inhalation (dust)		Human observation study			neurotoxic effects		Human	Experimental value
Inhalation			STOT RE cat.2	Brain	Brain affection			Expert judgement

## calcium sulfate

Route of exposure	Parameter	Method	Value	Organ	Effect	Exposure time	Species	Value determination
Oral (stomach tube)	NOAEL	OECD 422	79 mg/kg bw/day	Blood	No effect	35 day(s)	Rat (male)	Experimental value
Oral (stomach tube)	LOAEL	OECD 422	237 mg/kg bw/day	Blood	Change in the haemogramme/blood composition	35 day(s)	Rat (male)	Experimental value
Dermal								Data waiving

### **Conclusion**

Causes damage to organs (central nervous system, reproductive organs) through prolonged or repeated exposure if swallowed.

### **Mutagenicity (in vitro)**

## manganese dioxide

No (test)data available

## zinc oxide

Result	Method	Test substrate	Effect	Value determination	Remark
Negative with metabolic activation, negative without metabolic activation	OECD 471	Bacteria (S.typhimurium)	No effect	Experimental value	
Ambiguous	OECD 476	Mouse (lymphoma L5178Y cells)		Experimental value	

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# manganese dioxide

## lead(II)sulphate

Result	Method	Test substrate	Effect	Value determination	Remark
Negative with metabolic activation, negative without metabolic activation	Ames test	Bacteria (S.typhimurium)		Experimental value	

## manganese dioxide

Result	Method	Test substrate	Effect	Value determination	Remark
Negative with metabolic activation, negative without metabolic activation	OECD 471	Bacteria (S.typhimurium)		Experimental value	
Negative with metabolic activation, negative without metabolic activation	OECD 473	Human lymphocytes		Experimental value	

## calcium sulfate

Result	Method	Test substrate	Effect	Value determination	Remark
Negative with metabolic activation, negative without metabolic activation	OECD 471	Bacteria (S.typhimurium)	No effect	Experimental value	
Negative with metabolic activation, negative without metabolic activation	OECD 471	Escherichia coli	No effect	Experimental value	
Negative with metabolic activation, negative without metabolic activation	OECD 476	Mouse (lymphoma L5178Y cells)	No effect	Experimental value	

## Mutagenicity (in vivo)

### manganese dioxide

No (test)data available

### zinc oxide

Result	Method	Exposure time	Test substrate	Organ	Value determination
Negative (Intraperitoneal)	OECD 474		Mouse (male)	Bone marrow	Experimental value

### manganese dioxide

Result	Method	Exposure time	Test substrate	Organ	Value determination
Negative (Oral (stomach tube))	OECD 474		Mouse (female)		Experimental value

### calcium sulfate

Result	Method	Exposure time	Test substrate	Organ	Value determination
Negative (Oral (diet))	OECD 474		Mouse (male)		Experimental value

## Conclusion

Not classified for mutagenic or genotoxic toxicity

## Carcinogenicity

### manganese dioxide

No (test)data available

### zinc oxide

Route of exposure	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Oral (drinking water)	NOAEL	Carcinogenic toxicity study	> 22000 mg/l	52 week(s)	Mouse (male / female)	No carcinogenic effect		Read-across

### manganese dioxide

Route of exposure	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Unknown								Data waiving

### calcium sulfate

Route of exposure	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Oral (diet)	NOAEL	Carcinogenic toxicity study	256 mg/kg bw/day	104 weeks (daily)	Rat (male)	No carcinogenic effect		Experimental value
Oral (diet)	NOAEL	Carcinogenic toxicity study	284 mg/kg bw/day	104 weeks (daily)	Rat (female)	No carcinogenic effect		Experimental value

## Conclusion

Suspected of causing cancer.

## Reproductive toxicity

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# manganese dioxide

## manganese dioxide

No (test) data available

## zinc oxide

	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Developmental toxicity (Inhalation (aerosol))	NOAEC	OECD 414	7.5 mg/kg bw/day	14 days (6h / day)	Rat	No effect	Foetus	Experimental value
Maternal toxicity (Inhalation (aerosol))	NOAEC	OECD 414	1.5 mg/kg bw/day	14 days (6h / day)	Rat	No effect		Experimental value
Effects on fertility (Oral (stomach tube))	LOAEL (P)	Equivalent to OECD 416	7.5 mg/kg bw/day	22 weeks (daily)	Rat (male / female)	Reproductive performance		Read-across

## lead(II)sulphate

	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Developmental toxicity			category 1A					Annex VI
Effects on fertility			category 2					Annex VI

## manganese dioxide

	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Developmental toxicity (Inhalation (aerosol))	NOAEL	OECD 414	15 mg/m <sup>3</sup> air		Rat	No effect		Experimental value
Maternal toxicity (Inhalation (aerosol))	NOAEL	OECD 414	25 mg/m <sup>3</sup> air		Rat	No effect		Experimental value
Effects on fertility (Oral (drinking water))				13 week(s)	Rat (male / female)	No effect		Experimental value

## calcium sulfate

	Parameter	Method	Value	Exposure time	Species	Effect	Organ	Value determination
Developmental toxicity (Oral (stomach tube))	NOAEL	Equivalent to OECD 414	1600 mg/kg bw/day	10 day(s)	Rat	No effect	General	Experimental value
Maternal toxicity (Oral (stomach tube))	NOAEL	Equivalent to OECD 414	1600 mg/kg bw/day	10 days (gestation, daily)	Rat	No effect		Experimental value
Effects on fertility (Oral (stomach tube))	NOAEL	OECD 422	790 mg/kg bw/day	2 week(s)	Rat (male / female)	No effect		Experimental value

## Conclusion

May damage fertility or the unborn child.

## Toxicity other effects

### manganese dioxide

No (test) data available

## Chronic effects from short and long-term exposure

### manganese dioxide

ON CONTINUOUS/REPEATED EXPOSURE/CONTACT: Feeling of weakness. Loss of appetite. Loss of weight. Sleeplessness. Brain affection. Behavioural disturbances. Delusions. Disturbed tactile sensibility. Movement disturbances. Coordination disorders. Disturbed motor response. Tremor. Coughing. Respiratory difficulties. Risk of pneumonia. Change in the haemogramme/blood composition. Impairment of the blood forming system. Possible premature birth. Discolouration of the gums.

## 11.2. Information on other hazards

No evidence of endocrine disrupting properties

## SECTION 12: Ecological information

### 12.1. Toxicity

#### manganese dioxide

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity crustacea	LC50	US EPA	73.56 µg/l	48 h	Ceriodaphnia dubia	Semi-static system	Fresh water	Read-across
Long-term toxicity fish	EC10		17.8 µg/l	7 day(s)	Cyprinus carpio	Flow-through system	Fresh water	Read-across

Classification is based on the relevant ingredients

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# manganese dioxide

## zinc oxide

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	LC50		1.55 mg/l	96 h	Danio rerio	Static system	Fresh water	Experimental value; Lethal
Acute toxicity crustacea	EC50	OECD 202	1 mg/l	48 h	Daphnia magna	Static system	Fresh water	Experimental value; Zinc ion
Toxicity algae and other aquatic plants	IC50	OECD 201	0.136 mg/l	72 h	Pseudokirchneriella subcapitata	Static system	Fresh water	Experimental value; Growth rate
	NOEC	OECD 201	0.024 mg/l	72 h	Pseudokirchneriella subcapitata	Static system	Fresh water	Experimental value; Growth rate
Long-term toxicity fish	NOEC	OECD 215	0.039 mg/l - 0.974 mg/l	30 day(s)	Oncorhynchus mykiss	Flow-through system	Fresh water	Read-across; Lethal
Long-term toxicity aquatic crustacea	NOEC	OECD 211	0.04 mg/l	21 day(s)	Daphnia magna	Semi-static system	Fresh water	Read-across; Reproduction
Toxicity aquatic micro-organisms	EC50	OECD 209	> 1000 mg/l	3 h	Activated sludge	Static system	Fresh water	Experimental value; Respiration

## lead(II)sulphate

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	TLm		7.48 mg/l	96 h	Pimephales promelas			Literature study; Lead ion
Acute toxicity crustacea	LC50		0.3 mg/l	48 h	Daphnia magna			Literature study; Lead ion
Toxicity algae and other aquatic plants	EC50		0.14 mg/l		Selenastrum capricornutum			Literature study; Lead ion

## manganese dioxide

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	LC50	OECD 203	> 100 %	96 h	Oncorhynchus mykiss	Semi-static system	Fresh water	Experimental value; Saturated solution
Acute toxicity crustacea	EC50	OECD 202	> 0.073 mg/l	48 h	Daphnia magna	Static system	Fresh water	Experimental value; GLP
Toxicity algae and other aquatic plants	ErC50	OECD 201	> 100 %	72 h	Desmodesmus subspicatus	Static system	Fresh water	Experimental value; Saturated solution
Long-term toxicity fish								Data waiving
Long-term toxicity aquatic crustacea	NOEC	OECD 211	10 %	8 day(s)	Ceriodaphnia dubia	Static system	Fresh water	Experimental value; Saturated solution
Toxicity aquatic micro-organisms	EC50	OECD 209	> 1000 mg/l	3 h	Activated sludge	Static system	Fresh water	Experimental value; GLP
Toxicity sediment organisms								Data waiving

	Parameter	Method	Value	Duration	Species	Value determination
Toxicity soil macro-organisms						Data waiving
Toxicity soil micro-organisms						Data waiving
Toxicity terrestrial plants						Data waiving
Toxicity other terrestrial organisms						Data waiving
Toxicity birds						Data waiving

## calcium sulfate

	Parameter	Method	Value	Duration	Species	Test design	Fresh/salt water	Value determination
Acute toxicity fishes	LC50	OECD 203	> 79 mg/l	96 h	Oryzias latipes		Fresh water	Experimental value; Nominal concentration
Acute toxicity crustacea	LC50	OECD 202	> 79 mg/l	48 h	Daphnia magna		Fresh water	Experimental value; GLP
Toxicity algae and other aquatic plants	EC50	OECD 201		72 h	Pseudokirchneriella subcapitata			Experimental value; Greater than the water solubility
	NOEC	OECD 201	2.1 g/l	72 h	Pseudokirchneriella subcapitata			Experimental value; Greater than the water solubility
Toxicity aquatic micro-organisms	EC50	OECD 209	> 1000 mg/l	3 h	Activated sludge			Experimental value; Nominal concentration
	NOEC	OECD 209	1000 mg/l	3 h	Activated sludge			Experimental value; Nominal concentration

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# manganese dioxide

## Conclusion

Very toxic to aquatic life with long lasting effects.

## 12.2. Persistence and degradability

manganese dioxide

### Biodegradation water

Method	Value	Duration	Value determination
			Data waiving

## Conclusion

### Water

Biodegradability: not applicable

## 12.3. Bioaccumulative potential

manganese dioxide

### Log Kow

Method	Remark	Value	Temperature	Value determination
	Not applicable			

zinc oxide

### BCF fishes

Parameter	Method	Value	Duration	Species	Value determination
BCF		78 - 2060	14 day(s)	Oncorhynchus mykiss	Experimental value

### Log Kow

Method	Remark	Value	Temperature	Value determination
		1.53		Estimated value

lead(II)sulphate

### Log Kow

Method	Remark	Value	Temperature	Value determination
		1.13		Estimated value

manganese dioxide

### BCF other aquatic organisms

Parameter	Method	Value	Duration	Species	Value determination
					Data waiving

### Log Kow

Method	Remark	Value	Temperature	Value determination
	No data available			

calcium sulfate

### Log Kow

Method	Remark	Value	Temperature	Value determination
	Not applicable (inorganic)			

strontium sulphate

### Log Kow

Method	Remark	Value	Temperature	Value determination
	No data available			

## Conclusion

No straightforward conclusion can be drawn based upon the available numerical values

## 12.4. Mobility in soil

zinc oxide

### (log) Koc

Parameter	Method	Value	Value determination
log Koc		2.2	Literature study

## Conclusion

Contains component(s) that adsorb(s) into the soil  
Contains component(s) with potential for mobility in the soil

## 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

manganese dioxide

### 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)

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# manganese dioxide

zinc oxide

Groundwater

Groundwater pollutant

## SECTION 13: Disposal considerations

The information in this section is a general description. If available, the documentation for isolated intermediates will be attached in annex to support safe handling arrangements.

### 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 03 13\* (wastes from the MFSU of salts and their solutions and metallic oxides: solid salts and solutions containing heavy metals).

Depending on branch of industry and production process, also other waste codes may be applicable.

#### 13.1.2 Disposal methods

Recycle/reuse. 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 surface water (Directive 2000/60/EC, Council Decision 2455/2001/EC). Treat using the best available techniques before discharge into drains or the aquatic environment.

#### 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)

#### 14.1. UN number

UN number	3077
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#### 14.2. UN proper shipping name

Proper shipping name	environmentally hazardous substance, solid, n.o.s. (lead(II) sulphate)
----------------------	--

#### 14.3. Transport hazard class(es)


Hazard identification number	90
Class	9
Classification code	M7

#### 14.4. Packing group

Packing group	III
Labels	



#### 14.5. Environmental hazards

Environmentally hazardous substance mark	 yes
--	--

#### 14.6. Special precautions for user

Special provisions	274
Special provisions	335
Special provisions	375
Special provisions	601
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

### Rail (RID)

#### 14.1. UN number

UN number	3077
-----------	------

#### 14.2. UN proper shipping name

Proper shipping name	environmentally hazardous substance, solid, n.o.s. (lead(II) sulphate)
----------------------	--

#### 14.3. Transport hazard class(es)

Hazard identification number	90
Class	9

Reason for revision: 9.1

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Date of revision: 2021-11-10

Revision number: 0101

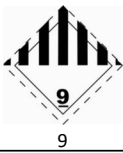
BIG number: 28902

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# manganese dioxide

Classification code	M7
---------------------	----

## 14.4. Packing group

Packing group	III
Labels	

## 14.5. Environmental hazards

Environmentally hazardous substance mark	 yes
--	--

## 14.6. Special precautions for user

Special provisions	274
Special provisions	335
Special provisions	375
Special provisions	601
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

## Inland waterways (ADN)

### 14.1. UN number

UN number	3077
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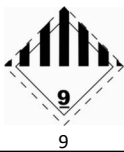
### 14.2. UN proper shipping name

Proper shipping name	environmentally hazardous substance, solid, n.o.s. (lead(II) sulphate)
----------------------	--


### 14.3. Transport hazard class(es)

Class	9
Classification code	M7

### 14.4. Packing group

Packing group	III
Labels	

### 14.5. Environmental hazards

Environmentally hazardous substance mark	 yes
--	--

### 14.6. Special precautions for user

Special provisions	274
Special provisions	335
Special provisions	375
Special provisions	601
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

## Sea (IMDG/IMSBC)

### 14.1. UN number

UN number	3077
-----------	------


### 14.2. UN proper shipping name

Proper shipping name	environmentally hazardous substance, solid, n.o.s. (lead(II) sulphate)
----------------------	--

### 14.3. Transport hazard class(es)


Class	9
-------	---

### 14.4. Packing group

Packing group	III
Labels	

# manganese dioxide

## 14.5. Environmental hazards

Marine pollutant	P
Environmentally hazardous substance mark	

## 14.6. Special precautions for user

Special provisions	274
Special provisions	335
Special provisions	966
Special provisions	967
Special provisions	969
Limited quantities	Combination packagings: not more than 5 kg per inner packaging for solids. A package shall not weigh more than 30 kg. (gross mass)

## 14.7. Maritime transport in bulk according to IMO instruments

Annex II of MARPOL 73/78	Not applicable
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## Air (ICAO-TI/IATA-DGR)

### 14.1. UN number

UN number	3077
-----------	------


### 14.2. UN proper shipping name

Proper shipping name	environmentally hazardous substance, solid, n.o.s. (lead(II) sulphate)
----------------------	--


### 14.3. Transport hazard class(es)

Class	9
-------	---

### 14.4. Packing group

Packing group	III
Labels	

## 14.5. Environmental hazards

Environmentally hazardous substance mark	
--	---

## 14.6. Special precautions for user

Special provisions	A158
Special provisions	A179
Special provisions	A197
Special provisions	A215
Special provisions	A97

### Passenger and cargo transport

Limited quantities: maximum net quantity per packaging	30 kg G
--	---------

## SECTION 15: Regulatory information

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

#### European legislation:

VOC content Directive 2010/75/EU

VOC content	Remark
	Not applicable (inorganic)

Prior informed consent (PIC)

Contains component(s) listed in Annex I of Regulation (EU) No 649/2012: Part 1 - List of chemicals subject to export notification procedure  
European drinking water standards (98/83/EC and 2020/2184)

lead(II)sulphate

Parameter	Parametric value	Note	Reference
Lead	5 µg/l		Listed in Annex I, Part B, of Directive (EU) 2020/2184 on the quality of water intended for human consumption.
Sulphate	250 mg/l		Listed in Annex I, Part C, of Directive (EU) 2020/2184 on the quality of water intended for human consumption.
Lead	10 µg/l		Listed in Annex I, Part D, of Directive (EU) 2020/2184 on the quality of water intended for human consumption.

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# manganese dioxide

## calcium sulfate

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 registration

This substance is handled under Strictly Controlled Conditions in accordance with Reach regulation Article 17(3) for on-site isolated intermediates and, in case the substance is transported to other sites for further processing, the substance should be handled at these sites under Strictly Controlled Conditions as specified in Reach regulation Article 18(4). Site documentation to support safe handling arrangements including the selection of engineering, administrative and personal protective equipment controls in accordance with risk based management systems is available at each manufacturing site. Written confirmation of application of Strictly Controlled Conditions should be available at the premises of every affected Distributor and Downstream Processor/User of the Registrants' intermediate.

### Information exposure scenarios

This safety data sheet does not contain an exposure scenario; exempted as (isolated) intermediate

### REACH Annex XVII - Restriction

Contains component(s) 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
· lead(II)sulphate	Lead sulphates; PbSO <sub>4</sub>	Shall not be placed on the market, or used, as substances or in mixtures, where the substance or mixture is intended for use as paint. However, Member States may, in accordance with the provisions of International Labour Organization (ILO) Convention 13, permit the use on their territory of the substance or mixture for the restoration and maintenance of works of art and historic buildings and their interiors, as well as the placing on the market for such use. Where a Member State makes use of this derogation, it shall inform the Commission thereof.
· lead(II)sulphate	Substances which are classified as reproductive toxicant category 1A or 1B in Part 3 of Annex VI to Regulation (EC) No 1272/2008 and are listed in Appendix 5 or Appendix 6, respectively.	Without prejudice to the other parts of this Annex the following shall apply to entries 28 to 30: 1. Shall not be placed on the market, or used, — as substances, — as constituents of other substances, or, — in mixtures, for supply to the general public when the individual concentration in the substance or mixture is equal to or greater than: — either the relevant specific concentration limit specified in Part 3 of Annex VI to Regulation (EC) No 1272/2008, or, — the relevant generic concentration limit specified in Part 3 of Annex I of Regulation (EC) No 1272/2008. Without prejudice to the implementation of other Community provisions relating to the classification, packaging and labelling of substances and mixtures, suppliers shall ensure before the placing on the market that the packaging of such substances and mixtures is marked visibly, legibly and indelibly as follows: "Restricted to professional users". 2. By way of derogation, paragraph 1 shall not apply to: (a) medicinal or veterinary products as defined by Directive 2001/82/EC and Directive 2001/83/EC; (b) cosmetic products as defined by Directive 76/768/EEC; (c) the following fuels and oil products: — motor fuels which are covered by Directive 98/70/EC, — mineral oil products intended for use as fuel in mobile or fixed combustion plants, — fuels sold in closed systems (e.g. liquid gas bottles); (d) artists' paints covered by Regulation (EC) No 1272/2008; (e) the substances listed in Appendix 11, column 1, for the applications or uses listed in Appendix 11, column 2. Where a date is specified in column 2 of Appendix 11, the derogation shall apply until the said date; (f) devices covered by Regulation (EU) 2017/745.
· lead(II)sulphate	Lead and its compounds	1. Shall not be placed on the market or used in any individual part of jewellery articles if the concentration of lead (expressed as metal) in such a part is equal to or greater than 0,05 % by weight. 2. For the purposes of paragraph 1: (i) "jewellery articles" shall include jewellery and imitation jewellery articles and hair accessories, including: (a) bracelets, necklaces and rings; (b) piercing jewellery; (c) wrist watches and wrist-wear; (d) brooches and cufflinks; (ii) "any individual part" shall include the materials from which the jewellery is made, as well as the individual components of the jewellery articles. 3. Paragraph 1 shall also apply to individual parts when placed on the market or used for jewellery-making. 4. By way of derogation, paragraph 1 shall not apply to: (a) crystal glass as defined in Annex I (categories 1, 2, 3 and 4) to Council Directive 69/493/EEC (*); (b) internal components of watch timepieces inaccessible to consumers; (c) non-synthetic or reconstructed precious and semiprecious stones (CN code 7103, as established by Regulation (EEC) No 2658/87), unless they have been treated with lead or its compounds or mixtures containing these substances; (d) enamels, defined as vitrifiable mixtures resulting from the fusion, vitrification or sintering of minerals melted at a temperature of at least 500 °C. (*) OJ L 326, 29.12.1969, p. 36. 5. By way of derogation, paragraph 1 shall not apply to jewellery articles placed on the

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# manganese dioxide

market for the first time before 9 October 2013 and jewellery articles produced before 10 December 1961.

6. By 9 October 2017, the Commission shall re-evaluate paragraphs 1 to 5 of this entry in the light of new scientific information, including the availability of alternatives and the migration of lead from the articles referred to in paragraph 1 and, if appropriate, modify this entry accordingly.

7. Shall not be placed on the market or used in articles supplied to the general public, if the concentration of lead (expressed as metal) in those articles or accessible parts thereof is equal to or greater than 0,05 % by weight, and those articles or accessible parts thereof may, during normal or reasonably foreseeable conditions of use, be placed in the mouth by children.

That limit shall not apply where it can be demonstrated that the rate of lead release from such an article or any such accessible part of an article, whether coated or uncoated, does not exceed 0,05 µg/cm<sup>2</sup> per hour (equivalent to 0,05 µg/g/h), and, for coated articles, that the coating is sufficient to ensure that this release rate is not exceeded for a period of at least two years of normal or reasonably foreseeable conditions of use of the article.

For the purposes of this paragraph, it is considered that an article or accessible part of an article may be placed in the mouth by children if it is smaller than 5 cm in one dimension or has a detachable or protruding part of that size.

8. By way of derogation, paragraph 7 shall not apply to:

- (a) jewellery articles covered by paragraph 1;
- (b) crystal glass as defined in Annex I (categories 1, 2, 3 and 4) to Directive 69/493/EEC;
- (c) non-synthetic or reconstructed precious and semi-precious stones (CN code 7103 as established by Regulation (EEC) No 2658/87) unless they have been treated with lead or its compounds or mixtures containing these substances;
- (d) enamels, defined as vitrifiable mixtures resulting from the fusion, vitrification or sintering of mineral melted at a temperature of at least 500 °C;
- (e) keys and locks, including padlocks;
- (f) musical instruments;
- (g) articles and parts of articles comprising brass alloys, if the concentration of lead (expressed as metal) in the brass alloy does not exceed 0,5 % by weight;
- (h) the tips of writing instruments;
- (i) religious articles;
- (j) portable zinc-carbon batteries and button cell batteries;
- (k) articles within the scope of:
  - (i) Directive 94/62/EC;
  - (ii) Regulation (EC) No 1935/2004;
  - (iii) Directive 2009/48/EC of the European Parliament and of the Council (\*);
  - (iv) Directive 2011/65/EU of the European Parliament and of the Council (\*\*)

9. By 1 July 2019, the Commission shall re-evaluate paragraphs 7 and 8(e), (f), (i) and (j) of this entry in the light of new scientific information, including the availability of alternatives and the migration of lead from the articles referred to in paragraph 7, including the requirement on coating integrity, and, if appropriate, modify this entry accordingly.

10. By way of derogation paragraph 7 shall not apply to articles placed on the market for the first time before 1 June 2016.

(\* Directive 2009/48/EC of the European Parliament and of the Council of 18 June 2009 on the safety of toys (OJ L 170, 30.6.2009, p. 1).

(\*\*) Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (OJ L 174, 1.7.2011, p. 88).

11. Doing either of the following acts after 15 February 2023 in or within 100 metres of wetlands is prohibited:

- (a) discharging gunshot containing a concentration of lead (expressed as metal) equal to or greater than 1 % by weight;
- (b) carrying any such gunshot where this occurs while out wetland shooting or as part of going wetland shooting.

For the purposes of the first subparagraph:

- (a) "within 100 metres of wetlands" means within 100 metres outward from any outer boundary point of a wetland;
- (b) "wetland shooting" means shooting in or within 100 metres of wetlands;
- (c) if a person is found carrying gunshot in or within 100 metres of wetlands while out shooting or as part of going shooting, the shooting concerned shall be presumed to be wetland shooting unless that person can demonstrate that it was some other type of shooting.

The restriction laid down in the first subparagraph shall not apply in a Member State if that Member State notifies the Commission in accordance with paragraph 12 that it intends to make use of the option granted by that paragraph.

12. If at least 20 % in total of the territory, excluding the territorial waters, of a Member State are wetlands, that Member State may, in place of the restriction laid down in the first subparagraph of paragraph 11, prohibit the following acts throughout the whole of its territory from 15 February 2024:

- (a) the placing on the market of gunshot containing a concentration of lead (expressed as metal) equal to or greater than 1 % by weight;
- (b) the discharging of any such gunshot;
- (c) carrying any such gunshot while out shooting or as part of going shooting.

Any Member State intending to make use of the option granted by the first subparagraph shall notify the Commission of this intention by 15 August 2021. The Member State shall communicate the text of the national measures adopted by it to the Commission without delay and in any event by 15 August 2023. The Commission shall make publicly available without delay any such notices of intention and texts of national measures received by it.

13. For the purposes of paragraphs 11 and 12:

- (a) "wetlands" means areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt,

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# manganese dioxide

		<p>including areas of marine water the depth of which at low tide does not exceed 6 metres;</p> <p>(b) "gunshot" means pellets used or intended for use in a single charge or cartridge in a shotgun;</p> <p>(c) "shotgun" means a smooth-bore gun, excluding airguns;</p> <p>(d) "shooting" means any shooting with a shotgun;</p> <p>(e) "carrying" means any carrying on the person or carrying or transporting by any other means;</p> <p>(f) in determining whether a person found with gunshot is carrying gunshot "as part of going shooting";</p> <p>(i) regard shall be had to all the circumstances of the case;</p> <p>(ii) the person found with the gunshot need not necessarily be the same person as the person shooting.</p> <p>14. Member States may maintain national provisions for protection of the environment or human health in force on 15 February 2021 and restricting lead in gunshot more severely than provided for in paragraph 11.</p> <p>The Member State shall communicate the text of those national provisions to the Commission without delay. The Commission shall make publicly available without delay any such texts of national provisions received by it.</p>
· lead(II)sulphate	The substances listed in column 1 of the Table in Appendix 12	<p>1. Shall not be placed on the market after 1 November 2020 in any of the following:</p> <p>(a) clothing or related accessories;</p> <p>(b) textiles other than clothing which, under normal or reasonably foreseeable conditions of use, come into contact with human skin to an extent similar to clothing;</p> <p>(c) footwear;</p> <p>if the clothing, related accessory, textile other than clothing or footwear is for use by consumers and the substance is present in a concentration, measured in homogeneous material, equal to or greater than that specified for that substance in Appendix 12.</p> <p>2. By way of derogation, in relation to the placing on the market of formaldehyde [CAS No 50-00-0] in jackets, coats or upholstery, the relevant concentration for the purposes of paragraph 1 shall be 300 mg/kg during the period between 1 November 2020 and 1 November 2023. The concentration specified in Appendix 12 shall apply thereafter.</p> <p>3. Paragraph 1 shall not apply to:</p> <p>(a) clothing, related accessories or footwear, or parts of clothing, related accessories or footwear, made exclusively of natural leather, fur or hide;</p> <p>(b) non-textile fasteners and non-textile decorative attachments;</p> <p>(c) second-hand clothing, related accessories, textiles other than clothing or footwear</p> <p>(d) wall-to-wall carpets and textile floor coverings for indoor use, rugs and runners.</p> <p>4. Paragraph 1 shall not apply to clothing, related accessories, textiles other than clothing, or footwear within the scope of Regulation (EU) 2016/425 of the European Parliament and of the Council (*) or Regulation (EU) 2017/745 of the European Parliament and of the Council (**).</p> <p>5. Paragraph 1(b) shall not apply to disposable textiles. 'Disposable textiles' means textiles that are designed to be used only once or for a limited time and are not intended for subsequent use for the same or a similar purpose.</p> <p>6. Paragraphs 1 and 2 shall apply without prejudice to the application of any stricter restrictions set out in this Annex or in other applicable Union legislation.</p> <p>7. The Commission shall review the exemption in paragraph 3(d) and, if appropriate, modify that point accordingly.</p> <p>(*) Regulation (EU) 2016/425 of the European Parliament and of the Council of 9 March 2016 on personal protective equipment and repealing Council Directive 89/686/EEC (OJ L 81, 31.3.2016, p. 51).</p> <p>(**) Regulation (EU) 2017/745 of the European Parliament and of the Council of 5 April 2017 on medical devices, amending Directive 2001/83/EC, Regulation (EC) No 178/2002 and Regulation (EC) No 1223/2009 and repealing Council Directives 90/385/EEC and 93/42/EEC (OJ L 117, 5.5.2017, p. 1).</p>

**National legislation Belgium**  
manganese dioxide

No data available

**National legislation The Netherlands**  
manganese dioxide

Waterbezwaarlijkheid	Z (2); Algemene Beoordelingsmethodiek (ABM)
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lead(II)sulphate

SZW - Lijst van voor de voortplanting giftige stoffen (ontwikkeling)	loodverbindingen, alle; Opgenomen in SZW-lijst van voor de voortplanting giftige stoffen (ontwikkeling); 1A
SZW - Lijst van voor de voortplanting giftige stoffen (vruchtbaarheid)	loodverbindingen, alle; Opgenomen in SZW-lijst van voor de voortplanting giftige stoffen (vruchtbaarheid); 2

manganese dioxide

SZW - Lijst van voor de voortplanting giftige stoffen (ontwikkeling)	Mangaan en -verbindingen; Opgenomen in SZW-lijst van voor de voortplanting giftige stoffen (ontwikkeling); 2
SZW - Lijst van voor de voortplanting giftige stoffen (vruchtbaarheid)	Mangaan en -verbindingen; Opgenomen in SZW-lijst van voor de voortplanting giftige stoffen (vruchtbaarheid); 2

**National legislation France**  
manganese dioxide

No data available

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# manganese dioxide

## lead(II)sulphate

Catégorie cancérogène	Plomb métallique et composés, en Pb
Catégorie toxique pour la reproduction	Plomb métallique et composés, en Pb

## National legislation Germany

### manganese dioxide

WGK	3; Classification water polluting based on the components in compliance with Verwaltungsvorschrift wassergefährdender Stoffe (VwVwS) of 27 July 2005 (Anhang 4)
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### zinc oxide

TA-Luft	5.2.1
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### lead(II)sulphate

TA-Luft	5.2.2/II
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### manganese dioxide

TA-Luft	5.2.2/III
TRGS900 - Risiko der Fruchtschädigung	Mangan und seine anorganischen Verbindungen; Y; Risiko der Fruchtschädigung braucht bei Einhaltung des Arbeitsplatzgrenzwertes und des biologischen Grenzwertes nicht befürchtet zu werden
	Mangan und seine anorganischen Verbindungen; Y; Risiko der Fruchtschädigung braucht bei Einhaltung des Arbeitsplatzgrenzwertes und des biologischen Grenzwertes nicht befürchtet zu werden

### calcium sulfate

TA-Luft	5.2.1
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## National legislation Austria

### manganese dioxide

No data available

## National legislation United Kingdom

### manganese dioxide

No data available

## Other relevant data

### manganese dioxide

No data available

### lead(II)sulphate

TLV - Carcinogen	Lead and inorganic compounds, as Pb; A3
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### manganese dioxide

TLV - Carcinogen	Manganese, elemental and inorganic compounds, as Mn; A4
	Manganese, elemental and inorganic compounds, as Mn; A4

## 15.2. Chemical safety assessment

No chemical safety assessment is required; registered as an isolated intermediate.

## SECTION 16: Other information

### Full text of any H- and EUH-statements referred to under section 3:

- H302 Harmful if swallowed.
- H332 Harmful if inhaled.
- H351 Suspected of causing cancer.
- H360 May damage fertility or the unborn child.
- H360Df May damage the unborn child. Suspected of damaging fertility.
- H372 Causes damage to organs (central nervous system, reproductive organs) through prolonged or repeated exposure if swallowed.
- H373 May cause damage to organs (brain) through prolonged or repeated exposure if inhaled.
- H373 May cause damage to organs through prolonged or repeated exposure.
- H400 Very toxic to aquatic life.
- H410 Very toxic to aquatic life with long lasting effects.

(*)	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

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# manganese dioxide

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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This annex contains information on risk management measures as specified in appendix 3 of the registration dossier for isolated on-site and transported intermediates

### **1. Brief description of technological process applied in manufacture of the intermediate EC 273-742-8**

- During the Zinc electrolysis, insoluble oxy-sulphates, (i.e. Lead- & calcium-sulphate and Manganese dioxide) can be formed at the Lead-anode surface ; part of it falls down in the cells another part sticks to the Lead-anode surface and is separated during the anode-cleaning steps
- The Pb-Mn cellmud is regularly collected from the bottom of the cells and from the anode-cleaning devices. It is settled, washed and filtered.
- Transfer of the Pb-Mn cellmud occurs in big-bags or containers or covered bulk load trucks, according to applicable regulation
- The 'Pb Mn cellmud' is a lumpy wet filtercake with an average Lead-content of 20-30% w/w and is typically used in production units of Lead metal (EC 231-100-4) or Lead compounds and recovery of precious metals
- Waste of the process:
  - None

### **2. Brief description of technological processes applied in use of the intermediate EC 273-742-8**

- The 'Pb Mn cellmud' is unloaded from transport trucks, ADR-big-bags or containers, ...and transferred to storage silo's through especially designed transfer units,
- The 'Pb Mn cellmud' is optionally blended with other Lead-containing primary or secondary materials
- The mixture is continuously fed to smelting furnaces (i.e. ISA, Blast furnace, ISF ...) or similar for further smelting extraction of lead and lead compounds, and precious metals
- Waste treatment:
  - None
  - During pyrometallurgical treatment: slag. The slag is dumped if not re-used in road filling.

### **3. Means of rigorous containment and minimisation technologies applied by the registrant during the manufacturing and /or use process**

#### **⇒ Description of the technical means to rigorously contain the substance**

- Process enclosures and closed circuits where relevant and possible
- Containment of liquid volumes in sumps to collect/prevent accidental spillage, acid solutions are treated adequately
- Potential dryers are operated under strong aspiration (negative pressure towards atmospheric pressure)
- All processes are performed in a confined area
- The process is managed and controlled from a separate control-room.

#### **⇒ Identification of residual emissions to workplace & environment**

Residual exposures at the workplace and the environment are assessed from regular measurements of dust/metals and represent usually a global exposure to several steps in a process. Dust control: dust and metals in dust needs to be measured in the workplace air (static or individual) according to national regulations.

- Workplaces: dust, metal concentrations?

# Annex to the Safety Data Sheet

## Slimes and Sludges, zinc sulfate electrolytic (273-742-8)

- Workers: biomonitoring – blood for Pb, twice a year if appropriate or according to regulation
  - Environment air: stack point source measurement (dust, metal concentrations)
  - Environment water: typically measured prior to discharge, if emissions to surface waters are relevant
- Some non-process waters can be generated containing Mn/Pb (e.g. from cleaning)

### ⇒ **Description of the procedural and control technologies to minimise emission and resulting exposure**

- The Pb Mn cellmud residue is kept moist, so dust formation/emission is by definition limited
- In the use phase, where it is dried, air emissions are controlled by use of air emission abatement devices e.g. filters, wet scrubbers. This may create a general negative pressure at the system openings (loading, sampling, production exit).
- regular sampling, cleaning, maintenance
- On-site waste water treatment techniques are applied to prevent releases to water (if applicable) e.g.: chemical precipitation, sedimentation and filtration.
- Local exhaust ventilation systems
- Special care for the general establishment and maintenance of a clean working environment by e.g.:
  - Cleaning of process equipment and workshop
  - Contained storage of leach residue in covered areas
- All residues formed during the leaching process (and gas-cleaning system at use site), are recovered and either recycled in the system or handled further according to waste legislation
- Wearing of gloves and protective clothing is compulsory
- With normal handling of the moist residue, no respiratory personal protection (breathing apparatus) is necessary.
- Eyes: safety glasses are recommended or compulsory

### ⇒ **Specification of management means and training that particularly contribute to the functioning of the technical means described above**

- integrated management system is implemented on the workplace e.g. ISO 9000, ISO ICS13100 series, ISO 1400X series, EMAS, or alike and, as usually applicable, by being IPPC-compliant (cf. NFM-BREF)
- housekeeping and hygiene procedures in place
- training provided for internal and external cleaning teams or technicians
- Follow up HS by medical unit: biomonitoring if required (e.g.. Pb, ...)

## **4. Means of rigorous containment and minimisation technologies recommended to the user of the intermediate**

- Means of containment and minimisation technologies are same as above
- Blending, and optionally pelletizing, and furnaces are operated under strong aspiration (negative pressure towards atmospheric pressure)
- The zinc leach residue is unloaded from [pneumatic] transport trucks, train, ADR-big-bags or containers, ...and transferred to storage zones or silo's through especially designed transfer units
- Material composition, handling, storage procedures and general guidance on safe use are communicated to the personnel or downstream (external) user by means of Safety Data Sheet

## 5. Special procedures applied before cleaning and maintenance

- Procedures are in place to ensure safe cleaning and maintenance operations
  - Stopping (part of) the process
  - Cooling down and proper ventilation of equipment
  - Switch off power supply & lock out procedure
  - Special PPE mandatory for cleaning personnel or maintenance technicians
  - Planning and training for internal and external personnel
- general guidance on safe use is communicated to the personnel or downstream (external) user by means of Safety Data Sheet

## 6. Describe activity and type of PPE in case of accidents, incidents, maintenance and cleaning activities

### Accident release measures:

- **Workers:** Immediately contact emergency personnel. Keep unnecessary personnel away.
- Use suitable protective equipment.
- **Environment:** Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers.
- **Cleaning:** If emergency personnel are unavailable, vacuum or carefully scoop up spilled material and place in an appropriate container for disposal by incineration. Avoid creating dusty conditions and prevent wind dispersal.

Fire: Use an extinguishing agent suitable for the surrounding fire. No specific hazard. Fire water contaminated with this material must be contained and prevented from being discharged to any waterway, sewer or drain. Thermal decomposition products are sulfur oxides (SO<sub>2</sub>, SO<sub>3</sub> etc.) and some metallic oxides. Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Periodic maintenance: (Furnace and associated equipment if applicable, Off-gas treatment system, Repair operations, Observational tasks and control activities), the following measures are taken:

- General protective and hygiene measures: Eating, drinking and smoking should be prohibited in areas where this material is handled, stored and processed. Workers should wash hands and face before eating, drinking and smoking. Separate storing of protective / work clothing is necessary. Avoid contact of spilled material and runoff with soil and surface waterways. Use process enclosures, local exhaust ventilation or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fumes or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.
- Respiratory protection: Use a properly fitted, particulate filter respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
- Hand protection: Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
- Eye protection : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists, gases or dusts.
- Body protection: Usual chemical work clothing.
  
- Cleaning activity : (Process equipment, workshop): same applies



## 7. Waste information

- The intermediate is a product for the production of zinc as a metal. If the normal processing route cannot be adhered to, returning it to the producer is recommended. Disposal should be in accordance with the official regulations (hazardous waste)
- PPE equipment is collected and disposed of
- Packaging?

# Annex to the Safety Data Sheet

## Slimes and Sludges, zinc sulfate electrolytic (273-742-8)

### Slimes and Sludges, zinc sulfate electrolytic (273-742-8) process scheme

Lifecycle of slimes and sludges is illustrated by the colored forms

