9.10 ES 8: Manufacture of cement

9.10.1 Exposure scenario

This generic exposure scenario describes the use of ferrous sulfate as an additive for the reduction of chromium (VI) content in cement. Solid ferrous sulfate is added as part of the formulation for dry cement. The addition of water to the dry mix, whereby the soluble ferrous sulfate and Cr(VI) species come into contact, is part of the use step and is considered as part of ES 9a, 9b and 9c (see following Sections).

9.10.1.1 Description of activities and processes covered in the exposure scenario

As cement is ordinarily a dry mixture, use of solid ferrous sulfate heptahydrate which has been dried to approx. 0.5% moisture (and/or contains an anticaking agent) or ferrous sulfate monohydrate in powder or granular form is recommended. Ferrous sulfate is said to be typically dosed either in the cement grinding mill feed or alternatively as the very last step in the production process (Kemira undated). However, another source said that ferrous sulfate cannot be added into the cement mill due to the extreme temperatures employed, ferrous sulfate being temperature sensitive. It describes an automated system for the dosing of ferrous sulfate into the cement as the last step prior to off-loading. This system is based on pre-existing silos and chutes and is flexible enough to allow addition at different levels to a range of different cement mixes which a plant may prepare (OAS 2009). Ferrous sulfate is added to cement at levels of approx. 0.5%.

There is a potential for airborne release of ferrous sulfate dust on charging and in preparing the mix (transfer, dosing), especially if containment is not good. Given the extreme hazard from dust in the cement industry it may be presumed that adequate ventilation and dust capture systems are in place. The MPA website indicates that “The industry operates highly efficient dust control systems on its factories that achieve 99.9% efficiency”. Any remaining workplace dusts may later be washed to water when the workplace area is cleaned down.

Regarding site size and distribution, the MPA website indicates that there are 14 major cement manufacturing sites in the UK. The MPA website statistics show that MPA cement production in the UK was approx. 10,100 kT in 2008. This suggests that approx. 720 kT cement are produced at a single site per year, equivalent to the use of approx. 3,600 t per year iron salt at the site. 350 days processing is assumed. This is approximately equivalent to 1,450 t Fe.

If it is assumed that dust formation leads to losses of a worst case 0.02 from the manufacturing floor, of which dust control measures recapture 99.9%, and the remainder settles and is washed to drain, this is equivalent overall to a release of 2E-05 from the site.

9.10.1.2 Operational conditions related to frequency, duration and amount of use

Table 9.10.1: Duration, frequency and amount – formulation

Information type	Data field	Explanation
Used amount of substance per day	4.1 t Fe/d	
Duration of exposure per day at workplace [for one worker]	Up to 8 hours	

Information type	Data field	Explanation
Frequency of exposure at workplace [for one worker]	Daily	
Annual amount used per site	approx. 1450 t Fe/y	
Emission days per site	350	

9.10.1.3 Operational conditions and risk management measures related to product[52] characteristics

Table 9.10.2: Characteristics of the substance or preparation

Information type	Data field	Explanation
Physical state	Liquid (aqueous solution) or Solid salts (assumed to be in granular/flake form rather than powdered)	Physical state at STP.
Risk management measures related to the design of product	Precautions against irritation	As necessary

9.10.1.4 Operational conditions related to available dilution capacity and characteristics of exposed humans

Table 9.10.3: Operational conditions related to respiration and skin contact

Information type	Data field	Explanation
Respiration volume under conditions of use	10 m^3/d	Default respiration volume for light work.
Area of skin contact with the substance under conditions of use	240 (PROC3) 480 (PROC4, PROC5, PROC8b, PROC9, PROC14) 960 (PROC8a)	ECETOC assumption for exposed skin surface area.
Body weight	70 kg	Default bodyweight for workers.

Please note that the respiration volume is accounted for when deriving the DNEL. See chapter R8 for details.

9.10.1.5 Other operational conditions of use

9.10.1.5.1 Consumers

Consumer end use of cement is assessed under ES 9c (refer to Section 9.12).

[52] "Product" includes substances, preparations and articles

Table 9.10.4: Technical fate of substance and losses from process/use to waste, waste water and air

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0	
Fraction of applied amount lost from process/use to waste water	2.00E-05	

9.10.1.6 Risk management measures

Comment:

It is noted that the hazards associated with other constituents of cements are generally anticipated to be significantly worse than the iron salts. PPE and other risk management measures mentioned here refer only to measures necessary to manage possible risks from iron salts. In view of the other constituents of formulated cements more rigorous RMM may be necessary and/or already in place.

Table 9.10.5: Risk management measures for industrial site

Information type	Data field	Explanation
Containment and local exhaust ventilation		
Containment plus good work practice required	Yes	
Local exhaust ventilation required plus good work practise	No	
Personal protective equipment (PPE)		
Skin protection	Protective gloves	
Eye protection	Safety glasses	
Clothing	Working clothing worn.	
Respiratory protection	If handling solid salts , Filter mask P2 (FFP2) must be used , in the absence of LEV	See Comment above
Breathing apparatus	None	See Comment above
Other risk management measures related to workers		
Procedural and control technologies	If handling solid salts, LEV OR containment and ventilation must be available.	See Comment above
Training. Monitoring/reporting and auditing systems	Equipment must be well maintained and cleaned daily.	See Comment above
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water		
Resulting fraction of initially applied amount in waste water released from site to the external sewage system		
Air emission abatement		

Information type	Data field	Explanation
Resulting fraction of applied amount in waste gas released to environment		
Onsite waste treatment		
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.		
Municipal or other type of external waste water treatment	Yes	
Effluent (of the waste water treatment plant) discharge rate	2000 m^3/d	
Recovery of sludge for agriculture or horticulture	Yes	

9.10.1.7 Waste related measures

Any solid wastes are ultimately assumed to be disposed of via landfill or incineration.
Details of the treatment of aqueous waste would vary at different sites but as a minimum the effluent treated in either in on-site or municipal secondary biological treatment plants prior to discharge.

9.10.2 Exposure estimation

9.10.2.1 Workers exposure

9.10.2.1.1 Short-term exposure

Short-term workers exposure is not relevant.

9.10.2.1.2 Long-term exposure

Modifications to the predicted exposures are only assumed where necessary to manage possible risks. Modifications are predominantly for use of personal protective equipment (PPE). The presence of local exhaust ventilation (LEV) is taken into account in scenarios where this is considered likely. The exposure levels from the ECETOC TRA model (2010) are used to estimate occupational exposure.

Dermal exposure
As described above, dermal exposure is most likely to occur through accidental spillage or during transfer and charging of storage and feed vessels where mechanical handling is not in place.
Dermal exposure estimates derived using the ECETOC TRA model can be found below. Note that the MPA website recommends the wearing of suitable eye protection, waterproof clothing, waterproof footwear and waterproof gloves when mixing and using cement.
Inhalation exposures

Transfer and charging of solid iron salts in powder or granular form could give the potential for inhalation. Inhalation exposure estimates derived using the ECETOC TRA model can be found below. It is assumed that PPE, LEV and mechanical handling would always be in place, given the hazardous nature of other cement ingredients besides $FeSO_4$.
The dermal and inhalation exposure estimates derived using the ECETOC TRA exposure levels are given in **Error! Reference source not found.**10.6.
Comment:
It is noted that the hazards associated with other constituents of cements are generally anticipated to be significantly worse than the iron salts. PPE and other risk management measures mentioned here refer only to measures necessary to manage possible risks from iron salts. In view of the other constituents of formulated cements more rigorous RMM may be necessary and/or already in place.

Table 9.10.6: Summary of highest long-term exposure concentration to workers

Highest value for relevant tasks.

Routes of exposure	Concentrations	Justification
Dermal local exposure (in µg/cm^2)	400 (PROC5, in absence of LEV)	The wearing of gloves is accounted for in this value
Dermal systemic exposure via contact with substance as such (in mg/kg bw/d)	0.7 (PROC4)	The limitation of 10% dermal uptake is assumed in deriving this value.
Dermal systemic exposure via aqueous solution (in mg/kg bw/d)	0.07 (PROC4)	The limitation of <1% dermal uptake is assumed in deriving this value.
Inhalation exposure	Negligible for contributing tasks that do not involve handling of solid products leading to evolution of dusts, or spraying of liquid product See also below	
Inhalation exposure (in mg/m^3)/8h workday[53] (refers only to any contributing tasks involving handling of solid products leading to evolution of dusts)	i) 1.8 (PROC8a, 8b).(LEV but no PPE) ii) 2.01 (PROC8a, 8b). Containment and mechanical/natural ventilation; and PPE (Filter mask P2 (FFP2)) must be used to limit exposure and manage risks. Equipment must be well maintained and cleaned daily.	i) Derived using Stoffenmanager scenario assuming handling of product with low speed or with little force in medium quantities ii) Derived using Stoffenmanager scenario assuming handling of product with low speed or with little force in medium quantities
Inhalation exposure (in mg/m^3)/8h workday[54] (refers only to any contributing tasks involving spraying of liquid product)	n/a	n/a

[53] air concentration at the workplace

[54] air concentration at the workplace

9.10.2.2 Consumer exposure

Consumers assessment for end use is set out in ES9c. Refer to Section 9.12.

9.10.2.3 Indirect exposure of humans via the environment (oral)

Refer to Section 9.2.1.

9.10.2.4 Environmental exposure

9.10.2.4.1 Environmental releases

A summary of the local releases of ferrous sulfate to air, waste water and industrial soil is given in Table 9..7 below.

Table 9.10.7: Summary of environmental releases

Life cycle stage	Formulation
Fraction in formulation	0.005
Number of days	350
Amount per day	~ 2.1kt cement equivalent to approx. 10 t per day iron salt (approx. 4.1 t Fe/day)
Fraction to air	-
Amount to air	0
Fraction to waste water (prior to WWTP)	2E-05
Fraction to sludge (passing to soil)	
Amount to waste water	0.08 kg/d
WWTP flow (default)	2E+06 l/d
Dilution in surface water (default)	10

Table 9.10.8: Summary of the releases to the environment

Compartments	Release from point source (kg/d) (local exposure estimation)	Justification
Aquatic (before WWTP)	0.08	
Air (direct + STP)	0	
Soil (direct releases only)	0	

Standard equations, described in detail in the REACH guidance and implemented within the EUSES 2.1 software, have been used to determine Predicted Environmental Concentrations (PECs) of Iron salts in surface water, seawater, sediment and agricultural soil.

Regional and continental background concentrations are also taken into account.

Table 9.10.9: Predicted Exposure Concentrations (PEC) for formulation

Compartments	Local PEC	Justification
Surface water (in mg/l)	2.4E-06	Calculated using EUSES 2.1.1 in accordance with the exposure scenario.
Freshwater sediment (in g/kg dwt)	45.0	Calculated using EUSES 2.1.1 in accordance with the exposure scenario.
Agricultural soil (in g/kg dwt)	50.0	Calculated using EUSES 2.1.1 in accordance with the exposure scenario.