9.11 ES 9a: Industrial use of cement

9.11.1 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 present in the dry cement. The addition of water to the dry mix, whereby the soluble ferrous sulfate and Cr(VI) species come into contact, may also be seen as a formulation step. Since this is performed at the location of use of the cement, releases are considered as part of professional/consumer use stages. Professionals or consumers are highly unlikely to formulate ferrous sulfate into cement; however, cement containing ferrous sulfate may be purchased and used by anyone.
At the end of the process, ferrous sulfate is no longer present. It is likely that exposure to the air, together with the alkaline nature of cement, results in conversion of any residual ferrous sulfate present to ferric oxides or hydroxides which are insoluble and bound into the cement matrix as it hardens. Any unused, waste dry cement mix is likely to be landfilled and, again, ferrous sulfate will be converted to insoluble ferric salts.

9.11.1.1 Description of activities and processes covered in the exposure scenario

"Industrial use" here does not imply use in an industrial setting as such but rather a larger scale and potentially better controlled workplace exposure environment.
Ferrous sulfate is added to cement at levels of *approx.*0.5%. Its presence is intended to alleviate the problems associated with exposure to soluble Cr(VI) which elicits allergic contact dermatitis. Cement is a hazardous substance in its own right with detailed occupational exposure controls being prescribed (Lafarge 2009). Any hazards to human health or the environment associated with the presence of ferrous sulfate are likely to be trivial compared with the hazards of soluble Cr(VI) or the alkaline nature of, or the dust hazard presented by, cement itself. In addition, it is likely that exposure to the air and the alkaline nature of cement results in conversion of any residual ferrous sulfate present to ferric oxides or hydroxides which are insoluble and bound into the cement matrix as it hardens.
There is some possibility for exposure to dust containing ferrous sulfate in opening bags, transferring, mixing etc. the dry cement mix but once water is added there is little chance for exposure and the likelihood of loss to waste water is negligible.

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

Table 9.11.1: Duration, frequency and amount

Information type	Data field	Explanation
Used amount of substance per day	40 tonnes cement mix containing 200 kg iron salt (approx. 80 kg Fe)	
Duration of exposure per day at workplace [for one worker]	Up to 8 hours	
Frequency of exposure at workplace [for one worker]	Daily	
Annual amount used per site	24 T Fe/y	
Emission days per site	300	

9.11.1.3 Operational conditions and risk management measures related to product[55] characteristics

Table 9.11.2: 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

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

Table 9.11.3: 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	480 (PROC5, PROC8b) 960 (PROC8a, PROC10)	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.

9.11.1.5 Other operational conditions of use

This scenario refers to use by building contractors on large building sites such as new housing developments, shopping centres etc.
Usage will often be outdoors with almost all waste solids responsibly collected and disposed of via municipal facilities (i.e. to specialist landfill), with some remaining solid wastes passing to local urban/industrial soil at the site of use. It would be expected that the iron would be immobile, not able to reach surface water or the wider environment. The possibility exists that in the worst case some dusts could be washed to waste water via storm drains, and from washing of clothing, tools etc. though it is to be expected that by the use of protective work-wear, dedicated equipment that such releases would be minimised.
Usage levels will be significantly larger because of the consumption of large quantities of concrete as well as mortar cements. This is presumed to be the largest form of end use. MPA usage statictics suggest that sales into larger scale professional use (based on figures for ready mix plus 'other' forms) constitute around 60% of consumption of cement. Around 90% of this is ready-mixed so there is no possibility of dust formation. The main site for local assessment should be assumed to be relatively large in the context of what is typical. In the absence of published evidence, it is assumed that this site is equivalent to 0.005 as a fraction

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

of the regional consumption at a single site. Under the previous system of exposure/risk assessment this fraction was known as the fraction of the main local source (fmls). Consumption at such a site would therefore be approx. 12,000 t cement over the course of a year. Assuming work progresses 300 days then this is equivalent to 40 tonnes cement per day.
If it is assumed that dust formation leads to losses of a worst case 0.02 from non-ready-mixed products, this is equivalent overall to a release of 0.002 from the site.

Table 9.11.4: 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	0.002	

9.11.1.6 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 9.11.5: Risk management measures for wide dispersive use

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

Information type	Data field	Explanation
Risk management measures related to environmental emissions from wide dispersive professional use		
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	

9.11.1.7 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.

9.11.2 Exposure estimation

9.11.2.1 Workers exposure

9.11.2.1.1 Short-term exposure

Short-term workers exposure is not relevant.

9.11.2.1.2 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 Table 9.11.6.

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 9.11.6: 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)	200 (PROC8b, 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)	0.6 (PROC10)	The limitation of 10% dermal uptake is assumed in deriving this value.
Dermal systemic exposure via aqueous solution (in mg/kg bw/d)	0.06 (PROC10)	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[56] (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[57] (refers only to any contributing tasks involving spraying of liquid product)	n/a	Derived using Stoffenmanager scenario assuming Handling of liquids at high pressure resulting in substantial generation of mist or spray/haze

9.11.2.2 Consumer exposure

Professionals and consumers assessment is set out in ES9b and 9c respectively. Refer to Section 9.12.

[56] air concentration at the workplace

[57] air concentration at the workplace

9.11.2.3 Indirect exposure of humans via the environment (oral)

Refer to Section 9.2.1.

9.11.2.4 Environmental exposure

9.11.2.4.1 Environmental releases

A summary of the local releases of ferrous sulfate to air, waste water and industrial soil is given in Table 9.1.7 below.

Table 9.11.7: Summary of environmental releases

Life cycle stage	Professional use – large scale
Fraction in formulation	0.005
Number of days	300
Amount per day	40 t cement mix containing 200 kg iron salt (approx. 80 kg Fe)
Fraction to air	-
Amount to air	0
Fraction to waste water (prior to WWTP)	0.002
Fraction to sludge (passing to soil)	
Amount to waste water	0.16 kg/d
WWTP flow (default)	2E+06 l/d
Dilution in surface water (default)	10

Table 9.11.8: Summary of the releases to the environment

Compartments	Release from point source (kg/d) (local exposure estimation)	Justification
Aquatic (before STP)	0.16	
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 9.11.9: Predicted Exposure Concentrations (PEC) for industrial use

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.