

9.3 Use of silver chloride as an intermediate in the manufacture of silver

Exposure Scenario Format (1) addressing uses carried out by workers

1. Title

Free short title	Use of silver chloride as an intermediate in the manufacture of silver
Systematic title based on use descriptor	SU14 PC19 (appropriate PROCs and ERCs are given in Section 2 below)
Processes, tasks and/or activities covered	Processes, tasks and/or activities covered are described in Section 2 below.
Assessment Method	The assessment of occupational exposure is based on measured data from the manufacture of silver metal. Environmental modelling was carried out in EUSES 2.1.

2. Operational conditions and risk management measures

Workplace	Involved tasks	Involved PROCs	ERC	REACH description
Handling of silver chloride	unloading of silver chloride from reaction tank or filter press, manual removal with shovels, storage in drums, unloading of drums into furnace, reaction tank or filterbox	26	6a	Use as an intermediate
Alternative I: Hot processes	furnace operation for the manufacture of silver, silver chloride is not available anymore after this process step	22		
Alternative II: Wet processes	reaction step for the manufacture of silver, silver chloride is not available anymore after this reaction step	4		
Cleaning and maintenance	manual cleaning, repair and maintenance operations, removal of residuals from e.g. filters/overspill or as waste	8a		

2.1 Control of workers exposure

Product characteristics

According to the MEASE approach, the substance-intrinsic emission potential is one of the main exposure determinants. This is reflected by an assignment of a so-called fugacity class in the MEASE tool. For operations conducted with solid substances at ambient temperature the fugacity is based on the dustiness of that substance. To determine the dustiness of a substance, a dustiness test may be performed. The rotating drum (modified Heubach) method can be used, to reflect potential dustiness during handling of a substance. In hot metal operations, fugacity is temperature based, taking into account the process temperature and the melting point of the substance. As a third group, abrasive tasks are based on the level of abrasion instead of the substance intrinsic emission potential. Although handling of aqueous solutions is usually associated with a very low emission potential, the spraying of aqueous solutions is assumed to be involved with medium emission. Further information can be found in the glossary of the MEASE tool (www.ebrc.de/mease.html).

Workplace	Use in preparation	Content in preparation	Physical form	Emission potential
Handling of silver chloride	not restricted		wet powder/filtercake (water content >30 %)	very low - low
Hot processes	not restricted		solid/molten	low - high
Wet processes	not restricted		solution	very low
Cleaning and maintenance	not restricted		wet splashes, wet powder/filtercake	very low - low

Amounts used

The actual tonnage handled/used per shift is not explicitly considered to influence the exposure as such for this scenario. Instead, the combination of the scale of operation (industrial vs. professional) and level of containment/automation (as reflected in the PROCs and technical conditions) is the main determinant of the process-intrinsic emission potential.

Frequency and duration of use/exposure				
Workplace	Duration of exposure (per shift/day)			
Handling of silver chloride	not restricted (480 minutes)			
Hot processes				
Wet processes				
Cleaning and maintenance				
Human factors not influenced by risk management				
The shift breathing volume covering all process steps is assumed to be 10 m ³ /shift (8 hours).				
Other given operational conditions affecting workers exposure				
Workplace	Room volume	Outdoor or indoor use	Process temperature	Process pressure
Handling of silver chloride	>1,000 m ³	indoors	ambient	not restricted
Hot processes			about 1,100°C	
Wet processes			ambient	
Cleaning and maintenance			ambient	
Technical conditions and measures at process level (source) to prevent release				
Workplace	Level of containment		Level of segregation	
Handling of silver chloride	not required		not required	
Hot processes	closed furnace		confined space	
Wet processes	closed reactor		not required	
Cleaning and maintenance	not required		not required	
Technical conditions and measures to control dispersion from source towards the worker				
Workplace	Level of separation	Localised controls (LC)	Efficiency of LC (according to MEASE)	Further information
Handling of silver chloride	not required	local exhaust ventilation	78 %	-
Hot processes		local exhaust ventilation	78 %	-
Wet processes		local exhaust ventilation	78 %	-
Cleaning and maintenance		not in operation	na	Appropriate cleaning devices avoiding emission of dust into air (such as vacuum cleaners) are required.
Organisational measures to prevent /limit releases, dispersion and exposure				
General good occupational hygiene practices are required to ensure safe handling of the substance. These include (i) measures to avoid any contamination of private households via the work-home-interface (e.g. shower and change clothes at end of work shift), (ii) good housekeeping practices in the workplace (i.e. regular cleaning with suitable cleaning devices and immediate cleaning in case of splashes and overspill), and (iii) measures to minimise inadvertent ingestion exposure (e.g. no eating and smoking in the workplace). In general, inhalation and ingestion of the substance should be avoided. Certified working clothing and shoes should be worn during work. In addition, the following principles should be followed: (i) ensure good general ventilation in the workplace, and (ii) do not blow dust (including dust remaining from dried splashes) off with compressed air. Regular training of workers in workplace hygiene practice and proper use of personal protective equipment is required.				

Conditions and measures related to personal protection, hygiene and health evaluation				
Workplace	Specification of respiratory protective equipment (RPE)	RPE efficiency (assigned protection factor, APF)	Specification of gloves	Further personal protective equipment (PPE)
Handling of silver chloride	not required	na	According to SCOEL, local dermal effects were not observed if workers operated in compliance with the inhalation OEL and direct contact with the substance was omitted. The use of gloves is obligatory if direct dermal contact with the substance cannot be excluded. In this case, protective gloves according to EN 374 should be worn and have to be changed according to manufacturer's information or when damaged, whatever is the earlier. Alternatively, thermal protective gloves should be used for hot processes.	standard working clothes (overall) and safety shoes
Hot processes	Depending on the type of conducted process, a face mask may have to be worn to protect against hot fumes.	no APF used in the calculation of inhalation exposure		
Wet processes	not required	na		
Cleaning and maintenance	not required	na		
<p>The use of personal protective equipment should always be seen as a last resort after operational conditions and further risk management measures have been improved.</p> <p>Any RPE as defined above shall only be worn if the following principles are implemented in parallel: The duration of work (compare with "duration of exposure" above) should reflect the additional physiological stress for the worker due to the breathing resistance and mass of the RPE itself, due to the increased thermal stress by enclosing the head. In addition, it shall be considered that the worker's capability of using tools and of communicating are reduced during the wearing of RPE.</p> <p>For reasons as given above, the worker should therefore be (i) healthy (especially in view of medical problems that may affect the use of RPE), (ii) have suitable facial characteristics reducing leakages between face and mask (in view of scars and facial hair). The recommended devices above which rely on a tight face seal will not provide the required protection unless they fit the contours of the face properly and securely.</p> <p>The employer and self-employed persons have legal responsibilities for the maintenance and issue of respiratory protective devices and the management of their correct use in the workplace. Therefore, they should define and document a suitable policy for a respiratory protective device programme including training of the workers.</p> <p>An overview of the APFs of different RPE (according to BS EN 529:2005) can be found in the glossary of MEASE.</p>				
2.2 Control of environmental exposure				
Product characteristics				
<i>Solid (powder), not biodegradable</i>				
Amounts used				
<p><i>Maximum site tonnage 92.7 tpa (as Ag)</i></p> <p><i>In the event this modelled tonnage is exceeded, please refer to section 4 of this scenario in which guidance is provided to enable manufacturers or downstream user to demonstrate on their operational conditions and implemented risk management measures are adequate.</i></p>				
Frequency and duration of use				
<i>Continuous use, 182 days/year based on SPERC factsheet 'Production v2.1'.</i>				
Monitored Emissions				
<i>No (generic default emissions applied based on SPERCs)</i>				
Annual measured tonnage emitted to air/water				
<i>Not applicable</i>				
Environment factors not influenced by risk management				
<i>Default data for receiving water and for the municipal sewage treatment plant are 18 000 m³/d and 2000 m³/d, respectively (resulting dilution factor to the receiving water 10). For marine assessments a default additional tenfold dilution is assumed.</i>				

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil		
<p>Air: No measured emission data. Emissions from SPERC factsheet 'Manufacture and recycling of massive metal and metal powders' v2.1'.</p> <p>Waste water: No measured emission data. Emissions from SPERC factsheet 'Manufacture and recycling of massive metal and metal powders' v2.1'. Assumed waste water goes to sewage treatment works in local freshwater assessment. Assumed waste water by-passes sewage treatment works in local marine assessment.</p> <p>Soil: No measured emission data. Emissions from SPERC factsheet 'Manufacture and recycling of massive metal and metal powders' v2.1'.</p> <p>Modelled release factors to air 0.03% water 0.002% before STP, soil 0%.</p>		
Conditions and measures related to municipal sewage treatment plant		
EUSES default STP with primary settler with effluent discharge rate 2000m ³ /d, serving 10000 inhabitants. Zero degradation assumed. Partitioning: 80.1% to sludge, 19.9 % to water calculated based on measured partition coefficients. Sludge assumed to be spread to agricultural land.		
Conditions and measures related to external treatment of waste for disposal		
<p>Hazardous wastes from onsite risk management measures and solid or liquid wastes from production, use and cleaning processes should be disposed of separately to hazardous waste incineration plants or hazardous waste landfills as hazardous waste. Releases to the floor, water and soil are to be prevented. If the silver content of the waste is elevated enough, internal or external recovery/recycling might be considered.</p> <p>Fraction of daily/annual use expected in waste: 0%</p> <p>Appropriate waste codes: 09 01 04*, 09 01 05*, 09 01 06*, 09 01 07, 09 01 08, 19 08 11*</p> <p>Suitable disposal: Hazardous waste produced during the manufacture and downstream use is sent to a recycler only marginal amounts are sent to a landfill or an incinerator. Waste containing silver is recycled for almost a 100%</p> <p>A detailed assessment has been performed on modelled and measured data and is reported in the Waste report (ARCHE, 2012)</p>		
Conditions and measures related to external recovery of waste		
<p>Waste generated under the form of sweeps, emission cleaning dusts and off spec material should be recycled into the manufacturing system.</p> <p>The focus of the silver industry is on the minimisation of waste by optimising the process and by utilizing residues and wastes as far as possible. The residues arising from different stages of the production process are therefore used as raw materials for other processes and an extensive network of metallurgical operators has been established for many years to increase the recovery of metals and eliminate the quantities of waste for disposal.</p> <p>With regards to the end of life, silver is fully recyclable and the silver content in the end of life material often determines the value of the waste.</p>		
3. Exposure estimation and reference to its source		
Occupational exposure		
<p>The assessment of occupational exposure is based on measured data from the manufacture of silver metal. The risk characterisation ratio (RCR) is the quotient of the exposure estimate and the DNEL (derived no-effect level) and has to be below 1 to demonstrate a safe use. For inhalation exposure, the RCR is based on a DNEL (long-term, local effects and systemic effects) for silver chloride of 0.13 mg/m³ (corresponding to 0.1 mg Ag/m³). This DNEL reflects the available indicative Occupational Exposure Limit (OEL) for poorly soluble silver compounds. A dermal DNEL was not derived as a threshold could not be derived for local effects. However, according to SCOEL, local dermal effects were not observed if workers operated in compliance with the inhalation OEL and direct contact with the substance was omitted. Thus, workers are sufficiently protected if operating in compliance with the inhalation DNEL of the substance and direct contact of the substance is omitted (protection against deposition of airborne dust on skin). The use of gloves is obligatory if direct dermal contact with the substance cannot be excluded (including protection against contaminated surfaces).</p>		
Workplace	Method used for inhalation exposure assessment (refer to introduction)	Inhalation exposure estimate (RCR)
Handling of silver chloride	measured data	0.0627 mg/m ³ (0.48)
Hot processes	measured data	0.0213 mg/m ³ (0.16)
Wet processes	measured data	0.1175 mg/m ³ (0.90)
Cleaning and maintenance	analogous data	0.0627 mg/m ³ (0.48)

Environmental emissions						
Environmental modelling was carried out in EUSES 2.1.1						
Local PEC						
Air mg/m ³ (RCR)	Fresh water mg/L (RCR)	Marine water mg/L (RCR)	Sediment freshwater mg/kg wwt (RCR)	Sediment marine water mg/kg wwt (RCR)	Soil mg/kg wwt (RCR)	STP mg/L (RCR)
2.12E-05 (NA)	1.92E-05 (0.809)	6.59E-06 (0.0154)	1.34 (0.0141)	0.547 (5.75E-03)	0.126 (0.183)	1.01E-03 (0.0405)
4. Guidance to DU to evaluate whether he works inside the boundaries set by the ES						
Occupational exposure						
<p>The downstream user (DU) works inside the boundaries set by the ES if the proposed operational conditions (OCs) and risk management measures (RMMs) as described in the exposure scenario (ES) are met (including substance/product characteristics). If the DU's conditions slightly deviate (such deviations are specified below) from the conditions as described in the ES, the DU may either inform the supplier of the substance to reflect the DU's conditions in a modified exposure scenario or has to ensure his slightly modified OCs and implemented RMMs are adequate. Depending on the basis for the exposure assessment (EA) conducted for the ES, this needs to be done in different ways:</p> <p><u>Use of measured data as basis for assessment:</u> If the EA in the ES is based on measured data, the same approach can be used at DU level. Please note that 6 measurements per workplace are required for an EA as a minimum. Depending on the variability of the data sets (expressed as the geometric standard deviation) and the level of the resulting risk characterisation ratio (RCR), additional measurements may be required. Only measurements of personal exposure of the inhalable fraction of airborne dust (according to EN 481) should be used. The exposure data shall either be applicable to the length of a specific task to be assessed or to a full-shift (i.e. sampled over a duration of at least 120 min) if the task to be assessed is conducted for a significant portion of the work shift. From the exposure data set the 90th percentile is to be used as a reasonable worst case (RWC) estimate for comparison with the relevant DNEL. RPE may be taken into account by applying the assigned protection factor applicable to the equipment used as given in EN 529:2005.</p> <p>It is noted that deviations from the ES are only allowed for the efficacy of installed RMMs (but not the type of RMM), exposure duration and personal protective equipment used.</p> <p><u>Use of exposure models:</u> If the EA in the ES is based on modelled data, the same model can be used to justify specific slight deviations from the conditions as described. All parameters needed to run the exposure estimation tool MEASE (available on www.ebrc.de/mease.html) can be found in the ES. It is noted that the installation of the described RMMs is mandatory and that exclusively the modification of the used PPE is allowed as deviation. The only parameters which may therefore be modified in the MEASE-calculation are consequently exposure duration, efficacy of the installed RMMs and PPE.</p> <p><u>Generic to both assessment bases:</u> Safe use is demonstrated, if the calculated exposure level is below the relevant DNEL (RCR <1). It is noted that smaller RCRs provide additional margin of safety and should therefore be envisaged.</p>						
DNEL _{inhalation} : 0.13 mg/m ³ (as silver chloride, corresponding to 0.1 mg Ag/m ³)						

Environmental emissions

The manufacturer with this ES (e.g. 92.7 tpa, 182 days and no emissions data) if, either:

A) Either the proposed risk management measures or conditions of use as described above are met or

B) The manufacturer can demonstrate on his own that his operational conditions and implemented risk management measures are adequate by reference to one or more of the following:

- 1) Where relevant measured ambient data in the receiving environment (obtained in accordance to the REACH guidance on monitoring data) demonstrate exposures are below the following PNEC concentrations:
PNEC_{freshwater}: 0.04 µg Ag/L (Soluble Ag)
PNEC_{marine}: 0.86 µg Ag/L (Soluble Ag)
PNEC_{sediment freshwater}: 438 mg Ag/kg dwt
PNEC_{sediment marine}: 438 mg Ag/kg dwt
PNEC_{soil}: 1.24 mg Ag/kg wwt
PNEC_{STP}: 0.025 mg Ag/L (Soluble Ag)

- 2) In the event the manufacturer has measured data available but not exactly those required as per REACH guidance, the manufacturer can still compare effluent concentrations with the following default emissions calculated for the default ES described above:

Concentration in untreated waste water released to freshwater STP must be < 6.67 µg Ag/L to ensure that the risk characterisation ratio does not exceed 1.

Concentration in untreated waste water released to marine water must be < 86 µg Ag/L to ensure that the risk characterisation ratio does not exceed 1.

The manufacturer may make use of an appropriate scaling tool such as MetalEUSES (free download: <http://www.arche-consulting.be/Metal-CSA-toolbox/duscaling-tool>) to estimate the associated exposure for other parameters than the default ones included here above to demonstrate safe use under this specific scenario or situation.

- 3) In case no safe use can be demonstrated under 1 or 2 above based on monitoring data, but the manufacturer has knowledge on emitted annual or daily loads, he can compare its emission to water to the emission ratio listed below:

The RCR will be equal to or lower than those stated above if they emit less than 0.0133 kg Ag/day to on site or off site waste water treatment works (equivalent to 0.0025 kg Ag/day to the receiving water).

- 4) In case the manufacturer does not have emission or ambient measured info he can use the Metal EUSES scaling tool (free download: <http://www.arche-consulting.be/Metal-CSA-toolbox/duscaling-tool>) to estimate the associated exposure for other parameters than those included here above to demonstrate safe use under this specific scenario or situation.