



Chlorine
0300

Annex: Exposure scenarios

ES2 - Exposure scenario – Industrial use of chlorine: end uses of substance as such or preparations at industrial sites

Use 2 Industrial use of chlorine: end uses of substance as such or preparations at industrial sites
<p>Sector of Use: SU5: Manufacture of textiles, leather, fur SU6b: Manufacture of pulp, paper and paper products SU8: Manufacture of bulk, large scale chemicals SU9: Manufacture of fine chemicals SU13: Manufacture of non-metallic mineral products SU14: Manufacture of basic metals SU16: Manufacture of computer, electronic and optical products</p>
<p>Process Categories: PROC1: Use in closed process, no likelihood of exposure PROC2: Use in closed, continuous process with occasional controlled exposure (e.g. sampling) PROC3: Use in closed batch process (synthesis or formulation) PROC4: Use in batch and other process (synthesis) where opportunity for exposure arises PROC5: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact) PROC8a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities PROC8b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities PROC9: Transfer of substance or preparation into small containers (dedicated filling line, including weighing) PROC13: Treatment of articles by dipping and pouring PROC14: Production of preparations or articles by tableting, compression, extrusion, pelletisation</p>
<p>Environmental Release Categories: ERC1: Manufacture of substances ERC4: Industrial use of processing aids ERC6b: Industrial use of reactive processing aids</p>
<p>Exposure Criteria: OELs : - 0.5 ppm (1.5 mg/m³) – 8 hr. TWA - 1.0 ppm (3 mg/m³) – 15 min. STEL</p>
<p>PNECs: Freshwater: 0.21 µg/L Marine water: 0.042 µg/L Intermittent releases: 0.26 µg/L, respectively.</p>

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Printed 26.01.2012
Revision 28.04.2011 (GB) Version 1.0

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No PNEC for soil was derived as no exposure is expected. No PNEC for sediment freshwater and marine water was derived as no exposure of the sediment is expected. PNEC _{STP} : 0.03 mg/L. PNEC oral: 11.1 mg/kg food.	
Processes, tasks, activities	Production of other chemicals (production, maintenance, sampling, loading and unloading); Waste water treatment; paper and textile industry
Exposure Scenario	
Contributing scenario (1) controlling environmental exposure for Use 2 Industrial use of chlorine: end uses of substance as such or preparations at industrial sites	
Industrial use of chlorine: end uses of substance as such or preparations at industrial sites	
Product characteristics	
Concentration: 100% Physical state: gas (liquefied)	
Amounts used	
10443 kt/y	
Frequency and duration of use	
Continuous release; 365 days/year	
Environment factors not influenced by risk management	
Dilution factor: 10 rivers, 100 costal zones (default)	
Other given operational conditions affecting environmental exposure	
Available chlorine in effluent is measured as total residual chlorine (TRC).	
Technical conditions and measures at process level (source) to prevent release	
There is practically no release to waste water and soil (upon contact with water chlorine is converted into sodium hypochlorite which is destroyed rapidly in contact with organic as well as inorganic material).	
Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil	
Immediately notify the appropriate authorities in case of gas spill. Do not discharge into the environment.	

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Organizational measures to prevent/limit release from site
All personnel are trained.
Conditions and measures related to municipal sewage treatment plant
Size of STP: 2000 m ³ /day (default)
Conditions and measures related to external treatment of waste for disposal
Waste treatment - Dispose in compliance with local/federal and national regulations - Absorb the product in an alkaline solution (caustic soda or sodium carbonate) - Reduce the product with sulfite, pyrosulfite or alkaline thiosulfate Packaging treatment -To avoid treatments, as far as possible, use dedicated containers. -Do not rinse the dedicated containers.
Conditions and measures related to external recovery of waste
None.
Contributing scenario (2) controlling worker exposure for Use 2 Industrial use of chlorine: end uses of substance as such or preparations at industrial sites
Manufacturing of chlorine
Product characteristic
Concentration: 100% Physical state: gas (liquefied)
Amounts used
Amounts used vary between mL (sampling) and m ³ (material transfer).
Frequency and duration of use/exposure
Duration [for one worker]: > 4 hours per shift (8 hours/day) Frequency [for one worker]: 220 days/year
Human factors not influenced by risk management
Respiration volume under conditions of use: 10 m ³ /8h-day (light activity) Body weight: 70 kg (worker).
Other given operational conditions affecting workers exposure
The production takes place in- and outdoors at ambient temperature.

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Technical conditions and measures at process level (source) to prevent release
<p>The opening of chlorine system takes place only after it has been emptied, purged, completely degassed, shut-off via blind flange and disconnected. In case of chlorine leaks, detection and monitoring are performed.</p> <p>Loading and unloading: Gaseous chlorine is transferred via pipelines to on-site users and chlorine is filled into the reaction vessel through closed systems, while off-gases from the reactor are treated before release to the atmosphere. When tankers or cylinders are used for smaller productions, the transfer of chlorine is done through loading stations adapted to the size of the vessel.</p>
Technical conditions and measures to control dispersion from source towards the worker
<p>Plants are equipped with chlorine detectors in different locations. They can generally detect 0.1 ppmV and have a pre-alarm level of 0.25 ppmV and an alarm level of 0.5 ppmV. The measuring device used for chlorine monitoring is an electrochemical sensor, which is sensible not only to chlorine, but also to other chlorinated substances present in the air. Chlorine concentration measured in the atmosphere of a Chlor-Alkali plant takes into account the exposure coming from the production of various substances (chlorine and, in most cases, other chlorinated chemicals).</p> <p>Sufficient air exchange and/or exhaust in work rooms. Appropriate exhaust ventilation at machinery.</p>
Organisational measures to prevent /limit releases, dispersion and exposure
<p>All personnel are trained. Safety procedures and protective equipment to be used to prevent dermal and inhalation exposure are dictated by the plant supervisor and documented in the work permit.</p>
Conditions and measures related to personal protection, hygiene and health evaluation



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Chlorine is produced in a closed system, and during normal working procedures, exposure to chlorine is possible only in case of leaks. Liquefaction, storage and loading areas are equipped with detectors. All workers in the plant receive specific training to react in a safe way in case of leaks. Personal Protective Equipment (PPE) is always used: safety glasses, safety shoes, long sleeved shirt, long pants, escape mask. In case of chlorine leaks, detection and monitoring are performed. Self-contained breathing apparatus are used for emergency operations.

Respiratory protection

- In case of emissions, face mask with type B cartridge.
- Self-contained breathing apparatus in medium confinement/insufficient oxygen/in case of large uncontrolled emissions/in all circumstances when the mask and cartridge do not give adequate protection.
- Use only respiratory protection that conforms to international/national standards.

Hand protection

- Protective gloves – chemical resistant
- Recommended materials: Neoprene (Non-recommended materials: PVC, polyethylene).

Eye protection

- Wear protective goggles for all industrial operations.
- If risk of splashing, chemical proof goggles/face shield.

Skin protection

- Overalls.
- Apron/boots of neoprene if risk of splashing.

Other precautions

- Shower and eye wash stations.
- Take off contaminated clothing immediately after work.
- Consult the industrial hygienist or the safety manager for the selection of personal protective equipment suitable for the working conditions

Dermal exposure

Because chlorine is not liquid but in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently no dermal exposure is to be expected. Moreover, the processes are closed and in case of opening of the system for maintenance purposes, safety procedures are applied in such a way that the opening of the system always takes place after complete degassing of chlorine. On the basis of a precautionary approach, the use of protective equipment such as face shield, goggles and gloves is mandatory in production area. This clearly indicates that there is no direct contact with liquid chlorine and, consequently, no dermal exposure.



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3. Exposure estimation and reference to its source

1. To estimate exposure to chlorine in end uses, two types of applications are considered :
2. The use as intermediate in chemicals production and the use in bleaching and water disinfection.
3. About 1% the chlorine production in EU is applied as the elemental chlorine in water applications such as drinking water, swimming pool, sewage treatment, pulp and paper and textile industry. The mentioned chlorine uses have strongly decreased, taking into account relevant tonnage (< 100 t/y); chlorine uses as intermediate are dominating.

■ Worker exposure

1. In case of the chlorine end uses as intermediate the productions worker exposure is limited taking into account that productions processes take place in closed system; exposure to chlorine is possible only in case of accident. Chlorine is filled into the reaction vessel through closed systems, while off-gases from the reactor are treated (generally by alkaline scrubbers) before release in the atmosphere. Unreacted chlorine at the end of the reaction is vented through an alkaline scrubber. Chlorine detectors are placed in the loading and in the degassing areas. Personal Protective Equipment (PPE) is always used: safety glasses, safety shoes, long sleeved shirt, long pants, escape mask. In case of chlorine leaks, detection and monitoring are performed. Self-contained breathing apparatus are used for emergency operation.

Maintenance:

2. The opening of chlorine system takes place only after it has been emptied, purged, completely degassed, shut-off via blind flange and disconnected. Maintenance and repairs of pumps, dosing systems and automatic control systems is only carried out by specialised companies or trained workers . In general maintenance work is carried out only if a "work permit" from the plant supervisor is issued when the status of the plant has been checked. In general, PPE used for handling of the product is: goggles, face shield, gloves, safety shoes, long sleeved shirt, long pants and gas mask. In case of opening of the system, PPE used is goggles, face shield, gloves, rubber overall, rubber boots, gas mask or self-contained breathing apparatus.

Sampling:

3. the sample is taken from the system at well identified sampling stations in the plant. Special sampling devices are used by trained persons with sufficient knowledge of all aspects of chlorine handling. Manual sampling is only done to check the reliability of the automated remote control systems. Protective equipment (safety shoes, long sleeved shirt, long pants, safety goggles, escape respirator) is used.

Loading and unloading:

4. when tankers or cylinders are used for smaller productions, the transfer of chlorine is done through loading stations adapted to the size of the vessel. All personnel who enter the area of a chlorine loading installation receive a special training and have available personal respiratory protection. A line diagram of the pipework and advice concerning the method of operation is permanently available. An emergency plan and precise instructions in case of emergency are permanently available and brought to the knowledge of the personnel



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involved. Self-contained breathing sets and protective clothing suitable for dealing with a chlorine leak are generally available in lockers located near the discharge point, and accessible at all times in case of emergency.

Other chlorine end uses :

- Drinking water
 5. When chlorine is used as disinfection agent for production of drinking water, it is supplied either in cylinders containing 60 to 100 kg chlorine or in special drums containing 600 to 1000 kg chlorine, depending on the size of the treatment plant. These containers are provided by specialised distributors. The cylinders or drums are kept in a well ventilated area, protected from rain, and access is limited to authorised and well trained personnel (locked zone). In most cases, an escape mask is at hand in the area.
 6. The replacement of an empty cylinder/drum by a full one is the key operation where exposure to chlorine could happen. Other occupational exposure to chlorine for workers handling the product in drinking water plants does not normally occur, as the product is added to water via closed circuits. The empty container is closed and the connecting circuit is placed under depression because the system is under chlorine demand.
 7. The new cylinder/drum is connected to the system through a flexible, stainless steel pipe and a new crushable joint to ensure a good tightness. The new cylinder/drum is then progressively opened and checked for possible leaks with an ammonia "detector". To reduce discontinuity in chlorine feeding during the change of cylinders/drums, they are connected to the system by pair, one being in use, while the other remains in standby. When the container in use is empty, a special valve system allows a quick change to the container in standby. The change of cylinders/drums occurs at a mean frequency of about once per week and the operation takes between 20 and 30 minutes. The loading area should be equipped with chlorine detectors.
- Waste water treatment
 1. Operations linked to the use of chlorine in waste water treatment and worker exposure a very similar as in case of drinking water
- Pulp and paper and textile industry
 2. Taking into account significant decreasing of those uses or by the sodium hypochlorite replacement
 3. the worker exposure description covered by EU Risk assessment Report for chlorine seems
 4. efficient enough

■ Environmental exposure

Essential influence for environmental exposure could be reported from the chlorine production sites and from the sites, where chlorine has end use as a intermediate, only. Total chlorine emission (release) from such industrial activity is estimating a bit higher as 100 t/y and globally, with the natural release comparison, this value does not account itself of the chlorine balance in the atmosphere and water.