From III Report 11606

Phosgene Safety Practices
for design, production and processing

Part 1
Key elements of safety practices - short version

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III caveat

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1 Phosgene safety management system

Central to phosgene safety is a comprehensive, well defined, communicated and enforced management system. The role of company and plant leadership in reinforcing the safety culture cannot be overstated.

- **Compliance with regulations:** The plant must comply with all local and national regulations. Company standards are normally followed if they are more stringent.
- **Planning:** In alignment with good operating practice, plans for plant design, operation and operator training should be clearly specified and communicated, preferably in written form.
- **Adherence to procedures:** Safe operation is ensured by adherence to procedures and rules that are audited, reviewed and updated on a regular basis.
- **Risk assessments:** An important technique for ensuring plant safety is conducting risk assessment reviews for the plant design and all changes. Tools for executing risk assessments are Inherent Safety Review, Hazard and Operability Process (**HAZOP**), Quantitative Risk Assessment (**QRA**) or company specific methods.
- **Root Cause Investigation (RCI):** Investigation of incidents and accidents, even if minor, by knowledgeable experts is important to the continuous improvement of safety systems. Conducting a documented RCI followed by implementation of necessary hardware, software and procedural changes in all documents and communicated to all personnel can be invaluable in preventing repeat occurrences.
- **Management of Change (MOC):** This process to review and approve all changes that are not like-for-like replacements before implementation whether regarding hardware, software, procedures or organisation is important.
- **Emergency response plans:** It is important to have an Emergency Response Plan for phosgene releases and personal exposure to phosgene. These plans typically include in-plant personnel, neighbouring plants and surrounding communities. Conducting regular drills is an effective way to check and maintain the effectiveness of these plans.
- **First aid and medical intervention:** As with other aspects of the safety program, advance planning, documented response protocols and training of medical response personnel ensure preparedness in the event of a phosgene exposure.
- **Safety strategy:**

  There are two basic principles which are considered to be very important:

  - The facility has established minimum managerial, procedural and technical requirements for the handling of phosgene
  - Safety solutions may be different depending on the product, process or other special or local requirements.

  Safety solutions employ primary and secondary safety measures:

- **Primary safety measure** (prevention): Primary measures are the use of technical design requirements along with the organisational and training requirements established in this manual
- **Secondary safety measures** (mitigation): Secondary measures are equivalent mitigation solutions providing backup in case of failure of primary measures and may include:
    - A containment chamber with a caustic scrubber
    - Fully jacketed equipment and piping systems
    - The use of a steam-ammonia curtain
    - Combinations of the three options above; or alternative mitigation systems.

2 Design criteria (basic engineering concepts)

2.1 Layout concepts

For a plant in proximity to occupied buildings (on-site and off-site), prevailing wind direction and traffic on site are important considerations.

Locating all equipment in phosgene service in close proximity will minimize hold up inventory; however, consideration should be given to safe operation and maintenance activities. Phosgene monitors installed strategically throughout the plant, the plant perimeter and the site fence-line are important safety tools.

2.2 Design concepts

Basic safety in this practice guide is the combination of primary followed by secondary measures and is important in the design of safe plant.

Consideration should be given to process conditions and primary and secondary containment (safety layers) to minimize the risk of phosgene being released to the environment.

For the design, consider provisions for all conceivable upset conditions.

2.2.1 Process conditions

- **No phosgene inventory:** in continuous processes advanced process control can eliminate the need for phosgene storage. For batch processes minimising the phosgene hold-up will reduce the risk of a significant release.
- **Temperature and pressure:** elevated pressures and temperatures are managed by applying adequate engineering standards.
- **Barrier fluid for heating and cooling**: instead of water / steam consider the use of inert process-compatible fluids for heating and cooling to exclude the possibility of water getting into the process, causing corrosion and other dangerous process conditions. If aqueous media are used additional precautions may be necessary.
- **Continuous chemical analysis:** Monitoring impurities continuously in raw materials can avoid dangerous process upset conditions.

2.2.2 Primary containment

Primary containment relates to the hardware of the plant, such as vessels, towers, exchangers, rotating equipment, piping and instrumentation.

- Careful consideration to the **temperature and pressure ratings** of process equipment is important, so that even under upset conditions their mechanical integrity is maintained.
- The choice of **materials of construction** is critical because water intrusion into the equipment can lead to severe corrosion or other dangerous conditions.
- To maximize mechanical strength **piping and nozzles** with minimum dimensions are good options, however **tubing** may not have the required strength to be used in phosgene service.

- **Screwed connections** may not be reliable enough to be used in phosgene service. Consider avoiding screwed connections, tubing and fittings in contact with phosgene, as non threaded process connections provide less potential for leaks.
- **Hoses**, braided or otherwise, may not be reliable enough to be used in phosgene service
- Minimise use of **flanges** as they represent a leak potential.
- Avoid using equipment subject to fatigue or which can easily break, like **expansion joints** or **sight glasses**.
- Minimize the use of **rotating equipment** (pumps, compressors, etc.) and consider gravity flow as an alternative.
- Seal less **pumps** (magnetically driven or canned motor pumps) are preferred.
- **Valves** of the bellows type with a second barrier are preferred.
- Paint applied to corrosion sensitive equipment will slow and reduce external corrosion.

2.2.3 Secondary containment

In case of a phosgene release from the primary containment the secondary containment is designed to contain the release.

Options for secondary containment are:

- A ventilated, completely enclosed **containment** chamber (enclosure) housing all of the equipment containing phosgene and equipped with a phosgene detection systems can be used to contain any release of phosgene. In the case of a release into the containment chamber the gases can be diverted to a phosgene destruction system. With the right equipment in place, such as analyzers for various chemicals (phosgene, carbon monoxide, etc.), cameras and safe entry procedures the containment chamber can be made accessible for personnel.
- Equipment and piping can be **jacketed** with the air space between the equipment/pipe and the jacket monitored for phosgene. In case of a leak the stream can be diverted to a phosgene destruction system.
- The equipment and piping of the unit containing phosgene can be surrounded by an automatically activated **steam–ammonia curtain** also called steam-ammonia wall. The aqueous ammonia completely decomposes the phosgene preventing escape beyond the plant perimeter.
  Proper design and operational measures are important, so that in case of an unintended release of phosgene existing regulatory value limits of ammonia are not exceeded.

2.2.4 Destruction / mitigation systems

Various options are available for systems which decompose and destroy phosgene during plant upset conditions. The design considerations for such systems are based on worst case scenarios, defined in a risk assessment, taking quantities, duration and stream composition into account.

Consistent with good operating practice, care should be taken to ensure that these decomposition systems, with a sufficient supply of neutralizing agent, remain fully operational under all circumstances in which phosgene is in the plant. A backup system is a good way to achieve this consideration. Emergency power for pumps, instrumentation and emission control analyzers is critical.

Two equivalent destruction / mitigation systems are commonly used:

- **Caustic scrubber**
  This is a packed caustic scrubber system fed with diluted caustic soda for phosgene destruction. Special attention directed to the design of the scrubber is important as high volumes of inert gases in the system may make the scrubber ineffective.
  Caustic soda can react with carbon dioxide coming out of the air and carbon dioxide liberated from the phosgene decomposition process. So it is important to monitor the caustic soda concentration.
- **Trickle bed towers with activated carbon**
  This decomposition system consists of a series of towers filled with activated carbon as a catalyst with a trickle system fed with water.

Phosgene destruction systems can be located outside the secondary containment because of the low concentration of phosgene in gaseous form.

2.3 Support / auxiliary systems

- **Segmentation:** Dividing the plant into smaller segments by installation of automated block valves allows for a quick depressurisation and dumping of a smaller section of the plant in case of an emergency.
- **Dump system:** A system with a dedicated vessel into which the contents of a process vessel can quickly be emptied in the event of a leak.
- **Blow down system:** A system with a dedicated vessel for collecting the emission of any activated pressure relief device,
- **Elephant-Trunk or spot-ventilation system:** A vacuum system designed to remove any residual fumes when opening lines or conducting other equipment during maintenance activities.

The discharges of the above systems are connected to a decomposition system.

- **Breathing Air System:** A dedicated, permanent breathing air supply system with numerous connection points to supply air to airline respirators when opening lines, breaking into equipment or doing maintenance where exposure to phosgene is possible.
- **Dedicated Nitrogen System for Phosgene systems:** A dedicated nitrogen system will prevent any phosgene from entering the plant nitrogen system in case of backflow.
- **Backflow protection:** Adequate design measures to ensure no phosgene enters any non phosgene areas of the plant.

2.4 Instrumentation and process control system

- The hardware, control valves, block valves, instrument piping, comply with the equipment criteria as defined in the original plant design and reviewed during Risk Assessments.
- An advanced, automated Distributed Control System (DCS) is the preferred option for process control
- Minimising operator interaction with the process control system will reduce the chance of operator error and increase the overall safety.
- Frequent auditing and maintenance of the hardware and the software will reduce the chance of malfunction.
- In normal operation the process control system will be in automatic mode avoiding manual operations. Bypassing interlocks can lead to extremely dangerous conditions. .

2.5 Electrical supply

Two independent 100% power supply lines coming from different sources with an automatic switch-over are an important consideration to ensure safe, uninterrupted plant operation.

If there is only a single electrical feeder power supply for critical systems and pumps, (i.e. rotating equipment necessary to safely shut down the plant, pumps for the scrubber systems, the process control system, phosgene alarm system, critical lighting), a backup supply provided by either diesel operated generators or/and batteries is encouraged.

2.6 Phosgene alarm and monitoring systems

A reliable phosgene monitoring system is advisable. A system employing multiple strategically installed detectors throughout the plant, which give both an audible and visual alarm in the control room if phosgene is detected is most effective.

It is advisable that a system is established that revokes all work permits in the event of a phosgene alarm, stopping all work immediately and providing all personnel in the plant with emergency instructions. Prior training typically includes information about predefined safe assembly points where all employees, contractors and visitors gather and can be accounted for.

Since wind direction and velocity is important for proper response in the event of a release, installation of wind indicating equipment in strategic locations is advisable.

As part of evaluating your company's own needs, the following considerations may be of assistance in case of a plant emergency:

- One or more safe assembly points
- An emergency coordinator to direct all personnel on the plant to a safe assembly point.
- A weather vane indicating wind direction and velocities in the control room with additional weather stations installed in other strategic locations. A system to quickly account for all personnel (operations, maintenance, lab personnel, service personnel, contractors, visitors) on the plant in case of a plant emergency.

2.7 Buildings

It is prudent to maintain a slight positive pressure in control rooms with a reliable and safe fresh air intake monitored for toxic gases including phosgene and other applicable chemicals. Activating an automatic shut down of the ventilation system based on the toxic gas monitor output is a good practice. Control rooms can also serve as "safe havens" in case of a phosgene release.

In case of an emergency the control room could become the emergency centre of the plant.

Adequate and sufficient personal protective equipment, which has been periodically inspected and well maintained, will normally be provided for all personnel operating or shutting down the plant and for evacuation purposes.

Good safety practice dictates that announcement systems and alarms be operational at all times so that they are always available during emergencies.

3 Operational criteria

3.1 Personal protection

It is useful to have the following items of Personal Protective Equipment (PPE) available in phosgene plants:

- Phosgene dose badges
- Hard hat
- Safety shoes
- Safety glasses and/or goggles
- Gloves of various types for different types of work
- Protective clothing, depending on the job to be executed
- Ear protection
- Escape mask
- Breathing air

Classifying personnel into the following categories according to their reason for being in an operating area is useful for managing PPE requirements:

- Permanent personnel assigned to the unit
- Company service and contractor personnel regularly working in phosgene areas
- Company service and contractor personnel infrequently working in phosgene areas
- Visitors

Different PPE requirements may apply to the above groups and will be specified by operations personnel.

Good operating practices suggest that minimum PPE requirements be specified for everybody and add-ons specified for all non routine jobs in the work procedures and on the work permit issued for each job.

It is strongly suggested that phosgene dose badges be worn at all times by all personnel in the plant to indicate whether they have been exposed to phosgene. It is important that the badge be worn close to the breathing zone so that an accurate reading of the amount potentially inhaled can be determined. In the case of phosgene exposure, the indicated dose can be used by the physician to specify the appropriate medical treatment.

3.2 Safety procedures

Because of the extremely hazardous nature of phosgene it is suggested that the area within a plant where phosgene is used be clearly defined, that strict operating discipline be strictly enforced and that written procedures be audited and updated routinely.

- **Work Procedures**: are a set of written procedures detailing routine and non routine work in the phosgene area.
- **Work Permit**: a work permit normally is issued by an authorised person for all work to be executed in the phosgene area with special emphasis on risk assessment, highlighting hazards, describing the PPE to be worn and other special requirements.

3.3 Training

It is prudent that a training programme be in place for:

- Operating employees
- Laboratory personnel
- Contractors
- Visitors

Including special training for new employees and refresher training for experienced operating personnel is an important consideration in such a program.

It is suggested that such training include periodic emergency drills and be updated regularly.

3.4 Sampling

Guidelines for taking samples:

- Minimising sampling will reduce the possibility of exposure.
- It is suggested that if phosgene-containing samples are taken, appropriate safety systems be in place to protect personnel from exposure and minimize the potential of any release to the environment.
- Use of supplied air respirators by personnel taking any phosgene-containing sample is advisable. This includes laboratory and pilot plant activities involving phosgene.

4 Maintenance and inspection

4.1 Maintenance

To ensure safe and uninterrupted operation of the plant, a documented maintenance process including preventative maintenance, repair and inspection of the equipment in the plant is prudent.

A contractor certification process may be necessary to ensure only qualified and trained personnel are selected.

It is not prudent to repair leaks in phosgene equipment that is in service, but it may be done if necessary in order to safely shut down the plant for a final repair and then only with appropriate approvals. A risk assessment may be useful to mitigate any risks involved.

4.2 Inspection and testing

Regular documented inspections of equipment either mandated by regulations or by company requirements, are useful for safe and reliable operation of the plant. It is prudent to test critical instrument shut downs, including fail safe options and interlocks on a regular basis.

5 Transportation

- Transportation of phosgene on- or off-site by rail or road is not advisable.
- A phosgene production unit integrated into the phosgene-consuming plant will reduce the likelihood of a release.
- When transporting laboratory scale quantities of phosgene or phosgene solutions, special precautions may need to be taken.

6 Abbreviations and acronyms

DCS	Digital Control System
HAZOP	Hazard and Operability Study
MOC	Management of Change
PPE	Personal Protective Equipment
QRA	Quantitative Risk Assessment
RCA	Root Cause Analysis
RCI	Root Cause Investigation