

## Industry: Chemical & Agro chemical Industry

1. **Application:** This standard is applicable for the manufacture, use and manipulation of Phosgene & phosgene-based products as Isocyanates, Phosgene & its derivatives.

**Phosgene: CoCl<sub>2</sub>**

**CAS No.: 75-44-5**

**UN No. 1076**

**Note: Phosgene is a chemical produced on demand and is not allowed for storage and cross-country transportation except only in small quantities for R&D purposes.**

### 2. Hazards:

These hazards may be classified as:

- (a) Physical, - potential to cause danger arising from slip/trip/falls, equipment operations where there can be excess noise, vibrations, heat radiations, etc. that are harmful to human, cause damage to personnel or fatal.
- (b) Chemical, - exposure to damage to humans arising out of handling chemicals or other hazardous materials such as Phosgene, Carbon Monoxide, Chlorine, Caustic, Ammonia, acids, alkalis, etc. that are used in the manufacturing process.
- (c) Biological, - exposure to chemicals and other toxic substances during the process of manufacture of phosgene in different stages, under different operating parameters that may affect the lungs, causes chronic or acute lung diseases, etc.
- (d) Ergonomic – man machine hazards such as HMI units, etc. depending on the process / operations, equipment and the persons involved in the operation.

**Equipment Selection & Safety Considerations:** Followings are some of the considerations that should be accounted during fabrication of equipment.

#### Pressure vessel Considerations –

- Fabrication of such vessel should be done only by approved vendors.
- It is advisable to design pressure vessels with a minimum number of connections to decrease the number of potential sources of leaks
- All vessels have to be designed for full vacuum
- It is recommended to design pressure vessel according to temperature and pressure conditions of operating plant. Corrosion allowance is to be added during calculation of wall thickness of vessels and connected nozzles.
- To protect vessel against high built up pressure, rupture disk and/or pressure relief valve should be attached with vessel having its outlet connected to phosgene scrubbing system or other suitable process equipment (e. g. surge vessel which can contain the pressure relief).
- Connecting flanges of vessel should be of type tongue & groove, raised face, flat face or any special design suitable for service of phosgene.
- All welds using at least 2 passes and butt welds that are full penetration welds welded with a cap weld pass if possible are optimal.

- Equipment that are designed for non-phosgene services should be avoided for phosgene service unless they are carefully inspected, tested and declared fit for use.
- MOC for vessel, pipelines and other attachments should be compatible with phosgene service at its operating conditions. Material with good ductility may be used.
- Phosgene service vessel should be tested internally / externally as per local and other governing laws and regulation. All the butt welds should be 100% radio graphed. Beside of that regular inspection schedule should be prepared and followed at company level.
- Good safety considerations require that pressure vessels be protected by adequate E&I instrumentation and/or with a pressure relief device that discharges to a phosgene destruction system in case the design pressure is exceeded.

**Heat Exchangers considerations** – heat exchangers should follow the same considerations that of pressure vessels as mentioned earlier.

Seamless tubes are recommended for fabrication of exchangers preferably roller expanded. Welded tubes should be radio graphed. Double tube sheet heat exchangers are recommended for phosgene services.

To avoid corrosion due to water being other media, periodic water analysis or monitoring should be carrying out employ corrosion inhibitors. An online pH monitoring system or conductivity monitoring system (preferred) should be installed for quality monitoring.

Air cooled heat exchangers should be avoided for phosgene services.

**Rotating equipment considerations** – pumps, compressors, agitator and vacuum pumps fall under category of rotating equipment. It is preferable to use seal less rotary equipment to avoid phosgene leakage.

- Casting area of equipment viz. has highest stress during operation, area which may have porosity or inclusion, have curvature, nearby area of flange should be radio graphed.
- Dye penetration, helium leak test is recommended for inspection of internal and external surfaces.
- Seal less pump or MAG drive pump are best suited equipment for phosgene services.
- As far as possible dead zones should be avoided inside the equipment as these areas are difficult to drain, purge or to be opened for cleaning.

**Centrifugal Pumps:** as mentioned earlier seal less MAG drive or canned pump should be used for phosgene service with instrumentation to monitor dry running of pump, dead heading, bearing flush backflow, motor winding temperature etc.

If double mechanical seal pumps are used, seal buffer fluid circulated between the seal, should be compatible with the process and at a higher pressure than the process pressure, will ensure that any inner mechanical seal leaks will go into the process and

not to the environment. The seal liquid level must be monitored and equipped with a low-level switch.

If a buffer fluid pot is used, monitoring of the level and pressure of the buffer fluid will indicate a seal leak. Dependent on the seal plan selection, it could do the same with a flow measurement.

**Compressors:** it is good to avoid use of compressors for phosgene services but if required then special design considerations are required.

**Vacuum pumps:** liquid ring pumps operated with solvent as a seal fluid is recommended for phosgene services. Used solvent fluid should be compatible with process conditions.

**Agitators:** It is important that the mounting flange, considered as part of the tank wall, be made of same construction materials as the tank. Other requirements are defined in the pump section

**Non-metallic equipment:** generally being used in small scale units. This type of equipment is suitable to handle aqueous liquids with organic components and other services that are corrosive in nature.

This equipment should be tested for healthiness of inner linings with well-established methods. Weld joints and its nearby area should be tested with spark testing method. The temperature rating of the lining material is critical.

**Glass vessels:** The use of equipment made of glass in phosgene service is not allowed except in laboratory applications due to the possibility of catastrophic failure.

**Glass lined steel vessel:** this type of vessels are typically used in fine chemicals and can be suitable for phosgene services also.

**Composite material / plastic lined steel vessel:** Steel equipment lined with ECTFE (Ethylene Chloro-Trifluoro-Ethylene) is most suitable for phosgene service that may be operated up to 100 °C. Above 100°C this material may deteriorate.

PVDF (Poly Vinylidene Fluoride) is considerably less suitable as a lining material for steel because of its poorer ability to process (higher stiffness), its high water vapor permeability and its high thermal expansion coefficient.

**Graphite heat exchangers:** heat exchanger made of graphite has been used for decades. If properly installed and operated, there are fewer chances of these exchangers to become defective.

Impregnated graphite is good choice for the material of construction for heat exchangers due to its high chemical resistance, good thermal conductivity and mechanical processing. Due to its passive surface, it is also less susceptible to contamination than metal.

**Piping System:** a piping system is defined as pipe, piping components including miscellaneous items contained within the system.

**Piping Design:** piping design should be as per national and other local regulations. Standard engineering practices should be followed. Followings are some of the criteria for optimal piping design.

- Metallic piping should be of specific schedule number. Seamless piping and its fittings are recommended for phosgene services.
- Piping having MOC of CS is accepted but higher alloy are recommended considering specific operational conditions.
- As far as possible threaded connections are to be avoided as they are more likely to leak. Phosgene carrying piping should be minimum of 1" NPS diameter is recommended. 1" NPS diameter is also recommended for instrument and sample connection flanges.
- Safety point of view, all the butt welds should be of two passes and 100% radio graphed. Use of expansion joints and flexible hoses are to be avoided.
- To reduce leakage possibility number of flanges, isolation valves, remotely operated valves etc. should be kept at minimum as far as practical.
- To avoid chances of corrosion of piping heating or cooling with water media is not advisable. Instead of that other process inert media should be used.
- Consider using either stainless steel or carbon steel with an appropriate coating for piping for vents, drains and miscellaneous connections which protrude through the insulation and are subject to icing and defrosting.
- Even if piping is going to be insulated it is advisable to apply paint on piping prior to insulate. Corrosion under insulation (CUI) must be considered when selecting piping materials of construction, paint system and insulation standards. Inspection program must be appropriate to detect this corrosion mechanism.
- It is recommended to follow standard color code for all the piping of phosgene.
- When not in use it is of good practice to end blind all the open flanges of vent, drain and other specific open points. This may help to reduce leak prone points of plant.

Generally, the following systems are **not suitable for phosgene piping in service** for isocyanate or polycarbonate:

- Thermoplastic lined metallic piping such as CS/PTFE; CS/PP etc. are not recommended for phosgene services due to requirement of frequent flange joints.
- Rubber lined piping are also not advisable for phosgene services due to poor performance of rubber liner whenever organic solvent is present with phosgene.
- PVC, CPVC etc. pipelines are also not recommended for phosgene service due to their poor strength against mechanical damage.

**Pipe routing and support:** phosgene piping should be laid down observing good engineering practices.

It is advisable to route piping that gives shortest distance between two equipment. To avoid accumulation of condensed phosgene, piping layout should be with minimum lowest points. A same criterion is also applicable for phosgene in liquid or dissolved form.

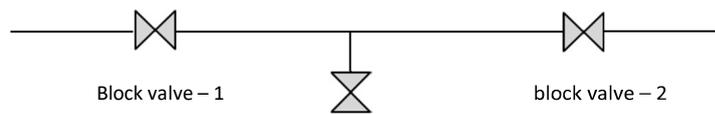
Phosgene carrying lines should be away from hot fluids or corrosive chemicals. This may help to avoid pressurization of line and external corrosion also.

Piping should be installed with proper support to avoid vibration, thermal expansion, stress etc. so as to reduce piping failure.

**Expansion joints:** to allow piping for thermal expansion it should be routed with adequate flexibility for that expansion loops may be used. But expansion joints like bellows or compensators should be avoided.

If expansion joints are unavoidable then piping should be adequately supported to lessen stresses. During installation, inspection and replacement manufacturer's guidelines should be followed.

**Double block and bleed:** The installation of double block and bleed valves allows the disconnection and opening of equipment from the live operating areas of the unit without a total shutdown of the whole unit. Double block valve with bleed valve is recommended for phosgene carrying piping.



**Non-metallic piping:** Piping made of non-metallic materials is suitable for handling aqueous and liquids with organic components or other services that are corrosive to metallic materials.

When selecting non-metals such as plastics it is important that the piping system is resistant to solvents or other chemicals that may be used. Since non-metallic material applications are in a constant state of development, assessment of material for each application including testing of a representative sample under process conditions is recommended.

**Valves:** only routine isolation valves are discussed here keeping safety relieving and that are being used for process analyser streams a side.

#### **Important considerations:**

- Minimum numbers of valves are preferable to avoid risk of leak. Valves may have flanged ends or butt welds ends.
- Valves should be designed for full vacuum and maximum process pressure and should be compatible with phosgene carrying piping also.
- Welded housing for valves should be avoided instead of that housing made of ductile material is recommended.
- Threaded connections in a valve body, Three way valve as block valve are not allowed for phosgene service
- Single body valves are preferred over split body valves.

**Recommended Valve types:** following types of valves are recommended for phosgene service

#### **Bellow sealed globe valve**

**Plug valves:** Plug valves have pressure and temperature limitations. Plug valves must be of lethal service design. Vented plugs are recommended for cold service plug valves to avoid thermal expansion.

**Butterfly valves** – This type of valves are used whenever large diameter of valve is required. Being acceptable for phosgene carrying service required modifications are to be made to conventional butterfly valves. (2 stuffing boxes with pressure monitoring of the inner space between the stuffing boxes).

**Ball valves** – These valves are widely used for phosgene service and particularly having presence of solid. Valves having metal seat will break trapped solid and will help to maintain sealing quality of material. It is recommended to drain ball valve completely and let trapped phosgene be released before dismantling valve body for any maintenance or inspection.

**Jacketed valves (secondary containment):** Standard jacketed valves that are providing of heating purpose are not suitable for phosgene service. Special considerations for monitoring the packing gland and bonnet joint are required for jacketed valves to be used for phosgene service.

**Gaskets:**

- some of the important considerations for use of gasket are compatibility of gasket material with process fluid, compatibility gasket material with process temperature and process conditions, type of flange where gasket is to be sandwiched.
- Recommended gasket material for metallic piping system is graphite gasket with or without metal reinforcement, spiral wound gasket with PTFE, kamm profile gasket with PTFE.
- Recommended gasket material for non-metallic system is rubber gasket with metal inserts, restructured PTFE gasket with non-asbestos fillers, PTFE gasket with memory insert, and graphite gasket without metal fillers.
- Points to be considered during installation of gasket are prior to fixing gasket closely examine surface for any damage, ensure alignment of surface and centering of gasket, use torque gun to tighten bolts in incremental rounds, take leak test after installation.

**Relief devices:**

- Vessels and piping must be protected against excessive pressure.
- It is most desirable to relieve the pressure to other process equipment. In cases where this is not possible, the exhaust (outlet) of the pressure relief valve must be directed to a phosgene decomposition system/Scrubbers designed to handle the flow rate and state of the worst credible scenario.
- In general, rupture disks must not be used as the primary relief device in phosgene service as they do not reclose after pressure relief).

If closed at both ends of a pipe section, block valves in cold service systems (e.g. phosgene solution or liquid phosgene) may cause an excessive pressure increase (thermal expansion). This must be avoided by one of the following options:

- One of the valves is conspicuously identified on P&IDs and locked in the open position.
- A pressure relief valve is installed around one of the block valves.
- Provide an expansion chamber (most often with a rupture disk) and pressure indicator that alarms in the control room.

As well as physical measures organizational and strict procedural controls may be just as effective.

#### **Pressure relief valve design details**

- All pressure relief valves in phosgene service must be spring-loaded with bellows. Balanced bellows are designed to eliminate the effect of back-pressure on the valve's relief setting.
- Additionally, bellows protect the valve components from contact with the product to prevent corrosion, fouling, etc. If the valve has a bonnet with a vent hole, it can be the manufacturer's standard connection (tapered threads) for the monitoring requirements since the connection will not see phosgene in normal service. The bellow has to be monitored for a failure.
- The inlet and outlet flanges of pressure relief valves should be consistent with the piping system design.
- As a minimum, pressure relief valves in phosgene service are required to have carbon steel bodies, stainless steel seats and trim, and hydroformed bellows).
- Certification of the bellows material is required. The bellows connection to the valve stem must be welded.

#### **Use of rupture discs:**

It is important to ensure that the product don't cause the pressure relief valves to stick. In locations where excessive corrosion, contamination or sticking is possible, pressure relief valves must be protected by rupture discs on the inlet and/or outlet sides. This protection is also an option in place of monitoring for bellows failure.

When rupture discs are installed, the void space between each disk and the valve seat must be monitored for disk failure

The relief valves need to be dried perfectly and installed in a way that moisture (moist air) cannot get in, otherwise they will fail in hours/days after introduction of phosgene (chlorine or HCL).

#### **Support and auxiliary system:**

**Segmentation:** It is practice of dividing large units into smaller sections with use of shut off valves that are remotely operated i.e. from the control room. Segmentation minimizes quantity of liquid phosgene that needs to be transferred in dump tank during leakage scenario.

Vapor space of each segmented area should connect with phosgene destruction system ensuring that no phosgene vapor goes to environment.

Segmentation practice minimizes amount of effort necessary to clean and prepare the area around leak to repair.

**Dump tank:** a dump tank is designed to contain the maximum quantity of the largest segment of phosgene handling system and should be connected with phosgene destruction system.

Phosgene draining to dump tank with help of gravity is ideal practice instead of using of pump. Phosgene system connected valves with that of dump tank should be remotely operated type.

It is advisable to flush phosgene draining line to dump tank with solvent once used. Dump tank should be kept empty and in ready to use condition.

**Blow down vessel:** It is advisable to lead discharge material of pressure relief valve to a separate vessel, known as blow down vessel where liquid and vapor phase may be separated from each other and connected with phosgene destruction system for further neutralization of phosgene vapours.

**Evacuation system:** It is a permanent system connected with phosgene destruction system and normally having double block and bleed valves for process side. Evacuation system is used for clearing equipment for maintenance and to make segmented area phosgene free in case of leakage.

**Elephant trunk system:** It is made of flexible hose having large opening and connected with (a dedicated) phosgene destruction system. Elephant trunk system mainly used to suck any of the phosgene vapours during opening of any flange, line or equipment. The phosgene destruction system of the elephant trunk system should not be connected with other phosgene destruction systems (e. g. maintenance, vent or process gas systems) to avoid backflow of phosgene and a possible phosgene release via the open ends of the flexible hoses.

**Breathing air system:** A dedicated and permanent breathing air supply system is to be provided from a secure source and safe source of supply. Breathing air system should be used whenever any maintenance activity or isolation activity is to be performed in phosgene handling plant. By using of breathing air system phosgene exposure may be avoided with greater extent. If a dedicated breathing air system is not installed, all maintenance or isolation activities must be performed by using SCUBA equipment.

**Nitrogen system:** to avoid backflow of phosgene to plant general nitrogen system, a dedicated nitrogen system (with adequate reverse flow protection) should be provided for phosgene handling sections

**Backflow prevention:** it is possible entering of phosgene to flushing system which is permanently connected with the phosgene handling equipment of section. To avoid backflow of phosgene appropriate pressure differential should be maintained between phosgene handling and flushing system. Valves connected to both systems should be closed on interlock whenever sufficient pressure differential is not maintained.

**Instrument and process control systems:** this section summarizes engineering and operational considerations for phosgene handling systems. It is advisable to purchase process controlling equipment from approved vendors only and adhering to all technical, legal and other engineering standards.

**Important considerations:**

**Construction principles and materials:** it is important that electrical and instrument equipment meet with the requirement of the pipe line to which they are mounted.

Instruments having active sensor systems and enhanced diagnostics are preferred such that if a sensor part is damaged a diagnostic alarm (e.g. maintenance needed, failure, etc.) is generated.

It is recommended that all pressure bearing butt welds, which are exposed to the phosgene medium during normal operations, be 100% radio graphed wherever practical.

It is good practice to test 100% of pressure bearing welds, other than butt welds (e.g. fillet welds), that are exposed to the phosgene medium by either dye penetration or magnetic particle testing.

**Analyzer instrumentation:** Analyzer instrumentation for phosgene service can be classified according to its purpose for monitoring of vent gases, perimeter monitoring and leak detection, of rooms and stream composition monitoring.

**Monitoring of vent gases:** Good options for measurement of phosgene are by infrared absorption or colour reaction with reagent solution on paper tape.

**Perimeter monitoring and leak detection:** The design of the monitoring system is based on the detection sensitivity, response time and monitor location.

The degree of monitoring is determined by the number and spatial distribution of the sample points or analyzers.

**Followings are two basic designs:**

- The "detector tube concept" where the gas samples are conveyed to one or more central analyzers via one or more lines, each having a number of sample points for monitoring certain areas of the unit or critical equipment. The test method is colour reaction with reagent solution on paper tape.

Note: Paper tape devices have negative cross sensitivity interference with HCl.

- The "individual analyzer concept" is one where each measurement point is an individual sensor or analyzer. Measuring method is with an electrochemical sensor.

**Air monitoring of rooms:**

For monitoring of ventilation systems in rooms that are manned with personnel on a continuous basis or for extended periods of time, a phosgene analyzer installed with the sample point in the fresh air inlet duct is advisable.

If phosgene is detected in the air intake, the safest option is to automatically shut off the air intake. And evacuate the personnel in the room to safety following the appropriate emergency procedures. The air intake system should have the possibility to flush it backwards, if phosgene had been detected in the system.

**Analyzer rooms,** which handle phosgene, should be equipped with the following items:

- Monitors for all potential hazards, e. g. phosgene, chlorine, Oxygen (low), CO and LEL (combustibility).
- An alarm panel showing alarm / status signals from each of the room air sensors and a status indicator for the ventilation system is recommended outside the room with repeater to the control room.

**Electrical supply:** Two independent 100% power supply lines coming from different sources with 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 lightning), a backup supply provided by either diesel operated generators or/and batteries is encouraged.

### **Building design:**

#### **Control room and safe rooms:**

It is advisable that control rooms and safe rooms/ safe havens be designed with the following features:

- 1) Location should upwind of the plant and as far as possible from sources of phosgene or other hazardous chemicals, which are toxic, flammable or explosive. Any entrance from an area with the potential for phosgene contamination having the characteristics of an air lock (two sealed doors in series in a small enclosed area) is good practice.
- 2) Gas-tight windows designed such that they may not be opened (except if designated as a fire escape) and preferably installed on the side of the building facing away from the unit.
- 3) No chemical lines, including compressed air (except breathing air) or nitrogen, running through the room, under the floor or in false ceilings.
- 4) Alarms and warning systems that are audible and visible in all rooms and buildings in a phosgene unit that announcement systems and alarms be operational at all times so that they are always available during emergencies.
- 5) 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.
- 6) 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.
- 7) Self-contained breathing apparatus or breathing air manifold supplied with compressed breathing air, sufficient for all personnel during the period of a safety shutdown of the plant and complete evacuation.

**Ventilation system:** It is good practice to locate the fresh air intake for the ventilation system upwind of the prevailing wind direction and away from potential sources of phosgene or other toxic and/or flammable substances.

Analysers to detect hazardous chemicals in the air intake that can activate an automatic shutdown of the ventilation system and an alarm to the control room if toxic gas is detected are advisable. Duplicate analysers could also be considered for increased safety.

Visual indication should be provided in the control room for monitoring of the status for all unit ventilation systems with automatic shutdown. It is prudent that the control

room has a manual means controlling the ventilation units to allow maintenance of the analysers.

**Alarm system:** It is advisable to inform and warn all personnel inside a unit when a phosgene emission is detected and, if necessary, to evacuate the plant. It is prudent, in an emergency situation that personnel outside the unit not be allowed to enter the unit without proper PPE.

Phosgene alarm systems will have a back-up power source (batteries, uninterrupted power supply, generators, etc.) to provide power for operating at least one hour after loss of the normal external power source.

**Announcement system:** a system of speaker should be provided to allow a unit announcement from the control room to the plant about any toxic release, action to be taken etc.

## **Process Safety:**

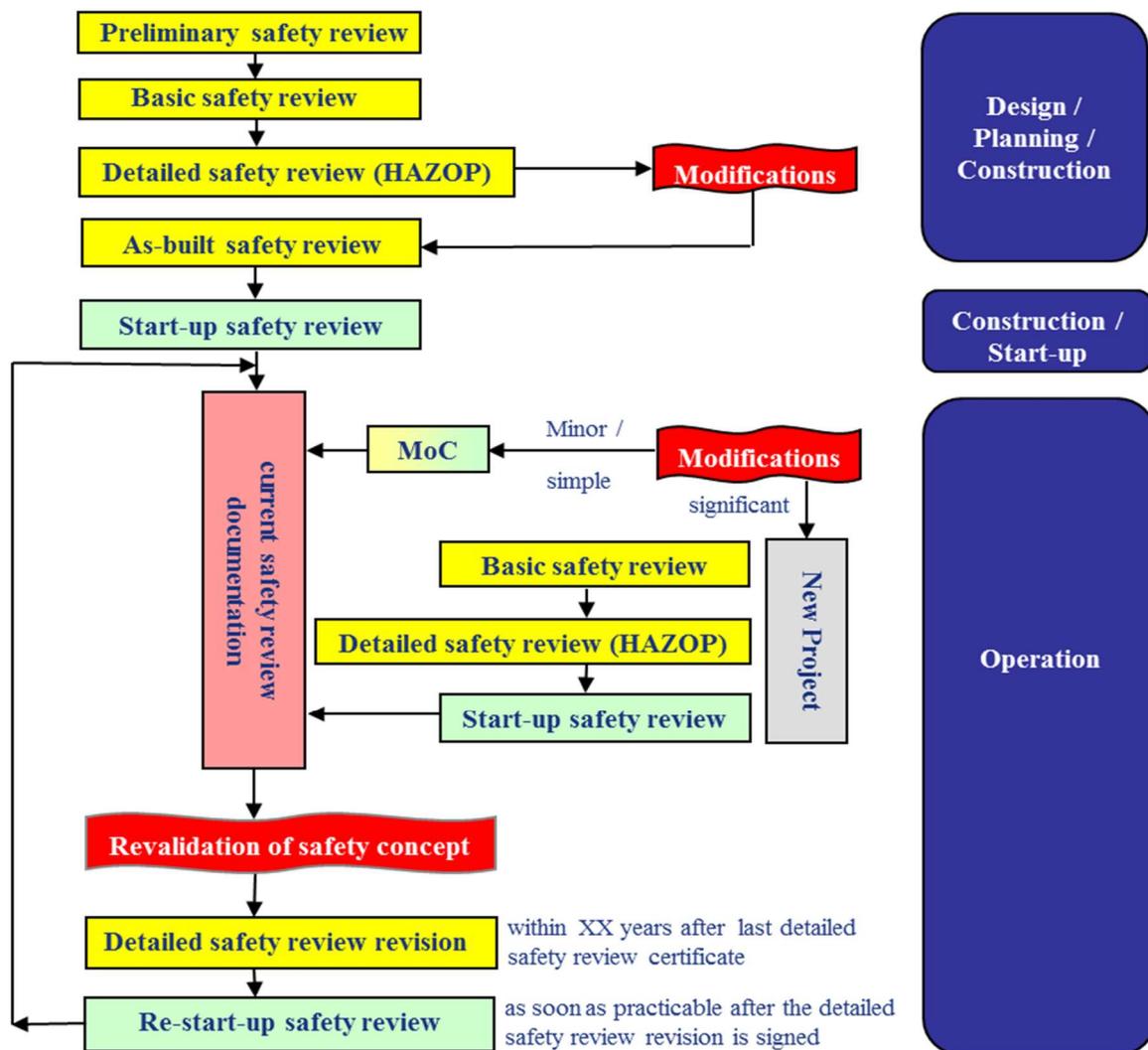
There shall be procedure for basic planning, methodology, technical and hardware requirement for execution of shut down activities safely and efficiently for both planned and unplanned shutdowns.

Pre-Start- Up Safety Review shall be conducted prior to installation of any new equipment.

Management of Change needs to be followed for installation of new equipment, modification of existing equipment, process or discard of unused equipment, etc.

Hazard identification studies such as QRA, PHA, HAZOP, HAZID, etc. whichever applicable, shall be conducted by a with an expert agency.

## Safety Review Flow chart



**Phosgene destruction systems / scrubber system:** Phosgene destruction systems/scrubber system should be designed considering the worst scenario of phosgene release along with the rate of release, time duration of release etc. It is important that phosgene destruction systems are functional during both normal operations and shutdown operations, as long as there is phosgene in the plant

Sources of phosgene during normal operations

The following phosgene-containing streams may need to be neutralized during normal operations:

- Off-gas from phosgene generation facilities
- Off-gas from phosgenation areas
- All other off-gas streams in the unit, e.g. off-gas from tanks, analyzers and other equipment
- Vacuum off-gas from distillation areas
- Other vent streams not mentioned above

### **Secondary safety measures**

Secondary containment is to prevent the dispersion of phosgene in the case of a failure of the primary containment. This is to protect personnel in the plant, in neighbouring plants and in the community beyond the site fence line.

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

**Secondary containment** is ventilated containment, also called chamber, enclosure or dome, housing the phosgene-containing equipment.

A ventilated, completely enclosed containment chamber or enclosure housing all of the equipment containing phosgene and equipped with a phosgene detection system, which 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.

### **Operational requirements:**

**Safe Operating Procedures:** it is of basic requirement to develop a Safe Operating Procedure (SOP) both for normal and abnormal working condition of plant by management considering national and international safety standards, safety philosophy etc. Safety procedures, instructions and methods should be prepared in co-operation with the people who are required to follow them.

Standard operating procedures should include procedures for:

- Start-up (e. g. after turnarounds or maintenance shutdowns)
- Shutdown (prior to turnarounds or maintenance activities)
- Rate changes
- Process upsets
- Response to process deviations
- Definition of key process parameters (including alarm and interlock settings)
- Definition of key process Safety parameters (including alarm and interlock settings)

### **Sampling:**

**General requirements:** Reduced sampling will minimize the potential for releasing phosgene to the environment. It is very important that when phosgene-containing samples are taken, appropriate safety systems are in operation and that written procedures are available and followed.

Proper PPE including supplied air is required for personnel taking any phosgene-containing sample, not only in production units but also in laboratories and pilot plants. Safety is increased when sample points are easily accessible, ergonomically sound and when spot ventilation is used to remove any escaping vapours.

**For liquid samples**, such as phosgene solutions, the best option for a sampling station is an enclosure (box) that is equipped with a venting system, connected to a phosgene destruction system, and a means to ensure that the venting system is working prior to taking any samples.

Self-contained sample stations with fixed volume samplers, have been used successfully and are considered excellent examples of a contained sampling station. It is important that the sampling process follows a written procedure that has been reviewed and approved for safety.

**Gas sampling:** It is recommended to analyse gas streams using online analysis and fixed pipe connections

**Phosgene solutions:** Minimize sampling of pure phosgene solutions (i.e. phosgene and solvent only) by using on-line analysis. If a phosgene solution must be sampled, the best way to obtain the sample is with a sampler that neutralizes the phosgene at the source.

### **Safety Procedures:**

Safety procedures should be in place for activities which are not covered by standard operating procedures. Special attention **should be decided on** all activities which must be performed in the phosgene work area of a plant.

It is important that instructions for working in phosgene service / phosgene work areas consider the following main elements:

- Appropriate personnel protection equipment (PPE) needed with respect to the hazard of the work
- Adequate instructions about the work to be performed, including risk evaluation
- Attendance of operating personnel for all line openings in order to respond to an unexpected situation or opening of wrong piping
- Attendance of a **safety guard during line breaking work** (It is recommended that the safety guard shall not be allowed to actively participate in the job!)

Standard procedure for de-Phosgenation, clearing and cleaning of phosgene containing equipment:

If equipment that has contained phosgene needs to be opened for maintenance, cleaning or inspection, proper preparation and decontamination is important to avoid phosgene emissions and unacceptable risk for the working personnel.

Standard detailed procedures for shutdown, de phosgenation and cleaning equipment in phosgene service are recommended

### **Permit to work System:**

It is important that a work permit be issued for all work where a primary barrier in the phosgene unit is opened. It is important that only authorized personnel issue work permits. In accordance with the dual-control principle, work permits should not be completed and signed by the same person.

Work permits (focus on phosgene) should assess the actual risk situation, especially in situations with increased risks.

### **Personnel training and qualification:**

It is important that the operation and maintenance of phosgene-generating and processing units be assigned only to well-trained and experienced operations and maintenance personnel.

It is strictly recommended that personnel are admitted to phosgene-producing or using plant only after receiving safety instruction and then only with the prescribed personal protective equipment (PPE). Phosgene badges are part of PPE and should be made readily available.

A unit-specific training is required for all new employees, which should involve details of the various physical, chemical and hazardous characteristics of phosgene as well as standard operating procedures of the phosgene equipment and processes. This training should include the following:

- Start-up procedures
- Shutdown procedures
- Normal operating parameters and procedures
- Consequences of operating outside normal operating parameters
- Emergency procedures / actions

It is important that the training plan include on-the-job training, consisting of specific unit operations for which competency should be demonstrated by the trainee. To provide this experience, special training in the form of table top drills, discussions with experienced operators, emergency drills or other means may be required.

When a scheduled shutdown is planned, consideration should be given to ensuring that employees with experience of certain operations (start-up, shutdown and preparation of maintenance work) are available.

### **Ongoing training for employees who operate phosgene-containing equipment**

Once an employee has been certified to operate phosgene-containing equipment, table top exercises that pertain to unit operations and upset conditions for phosgene-containing portions of the unit should be performed to enhance operating skills on a regular basis.

### **Training for employees (company or long-term contractors) who maintain phosgene-containing equipment**

It is important that the maintenance of phosgene-generating and processing units be assigned to well-trained, experienced and certified maintenance personnel. Prior to beginning work in the phosgene unit, it is important that all personnel have been instructed about:

- The potential hazards of working in a phosgene area
- Aspects of the work planned
- The planned response in the event of a release or other emergency

They must also be issued with the proper PPE and ensure that their escape device is in proper working condition.

**It is advisable that contract employees, who are used in the same role as company technicians, should obtain the same training as company employees.**

### **Visitors training**

Important considerations for visitors to phosgene-operating areas prior to entering the area:

- Inform visitors of the basic characteristics of phosgene (smell, gas density, etc.).

- Issue phosgene indicator badges to visitors and inform them about the proper use and care of them.
- Instruct visitors about the general alarm plan for the area they are visiting as well as exit/evacuation procedures. This can be accomplished by means of a safety video or a safety briefing.
- Instruct visitors on the use of the escape device used by the area being visited.
- Assign unit personnel to accompany visitors and take responsibility for their safety.

### **Emergency Preparedness and Response:**

Management should have prepared an Emergency Preparedness and Response (EPR) plan for an unfortunate event of phosgene releases and any emergency situations arising post release of it. A comprehensive EPR should contain all the information and what to do instruction in case of on-site or off site emergency. Effectiveness of EPR should be checked by carrying out mock drills at regular intervals of time.

Table top drills to be used to train company and contract employees to create awareness about emergency preparedness and response.

It is recommended to develop the scenario of effect of leakage by dispersion modelling and consider the responses in case of emergency preparedness.

The following considerations may be of assistance in case of a plant emergency:

- One or more safe assembly points are needed so as to ensure that at least one assembly point is not downwind from the phosgene emission point.
- Emergency coordinators to direct all personnel on the plant to a safe assembly point.
- A weather vane which indicates wind direction and velocities in the control room.
- A system for head count of all personnel (operations, maintenance, lab personnel, service personnel, contractors, visitors) on the plant in case of a plant emergency.

### **Medical assistance:**

Phosgene producing facilities should have adequate numbers of First Aid centres or Occupational Health Centres. Timely administered first aid to victims of phosgene exposure is of much importance. Management should also focus to train as many as possible first aiders. Antidotes & specific medicines stocks are maintained at OHC.

### **Personal protection**

Besides the usual protective equipment (e.g. safety shoes, adequate gloves, safety glasses or goggles, work suits, in some situations coveralls), respiratory protection in 4 levels is key for personal protection.

- Level 1: Escape masks

It can be considered that each worker carry an escape mask, although the strong recommendation is for filter masks. Visitors to a phosgene plant must always carry an escape mask.

Level 2: Filter masks

Each worker should have a personal filter mask with a cartridge giving protection from phosgene for the time required to escape from a contaminated area, at least for 5 minutes. The filter masks and cartridges must be regularly checked and replaced if necessary.

Level 3: Breathing air lines

For routine work potentially involving opening lines, flanges or vessels, a breathing air system for use with full-face masks can be installed throughout the plant

Level 4: SCBA.

For emergencies, and also for routine work potentially involving breaking containment if no breathing air system has been installed, SCBA is mandatory.

### **Workplace air monitoring and badges**

Continuous air monitoring in phosgene plant

- Various sniffers / phosgene detectors at strategic locations connected to DCS with plant tripping interlock
- Portable phosgene detector
- Ammonia torch for better detection

### **Phosgene badges**

Specifically, for phosgene there are medical badges available that show the dose of exposure.

There are several makes of badges available on the market. They all rely on a colour reaction. When choosing a badge, it is important to make sure that the badge covers the medically important range.