KLJ Organic Qatar W.L.L.

Process Safety Management in Chlor-Alkali Industry

Venue :Gulmohar Hall, India Habitat Centre, New Delhi

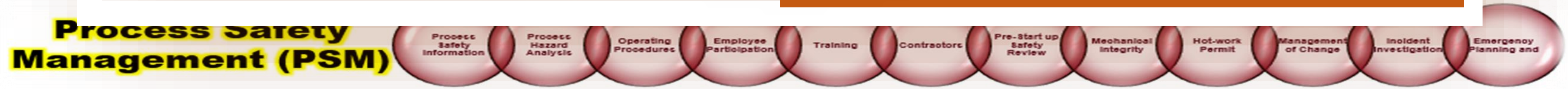
Date : 12 November 2024

Time : 02.10 PM (IST)

Place : Delhi

By Mr. Manish Srivastava

1. PSM-Introduction



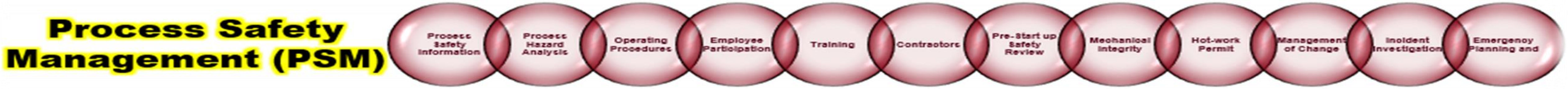
Process Safety Management in Chlor-Alkali Industry

PSM is management systems and controls (programs, procedures, audits, evaluations) applied to a manufacturing process in a way that process hazards are identified, understood, and controlled so that process related injuries and incidents are prevented.

Process → handling, manufacturing & storing of chemical

Process safety → operation of facilities that process hazardous chemicals free from episodic or catastrophic incidents

Process safety management → application of management systems to identification, understanding & control of process hazards to prevent catastrophic incidents



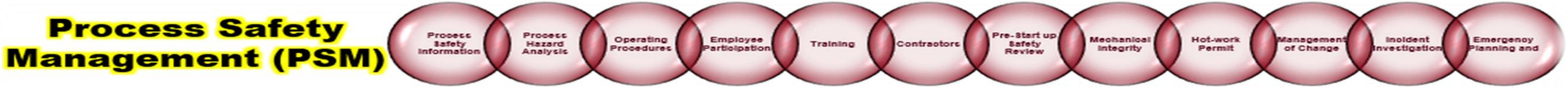
Process Safety Management in Chlor-Alkali Industry

Why PSM: Zeroth Law of Productivity

The productivity of any facility drops immediately to zero, if it:

- Blows up
- Burns down
- Impacts the community or is
- Shut-down for violating regulations

Incidents like the Bhopal disaster (1984) as key examples.



Process Safety Management in Chlor-Alkali Industry

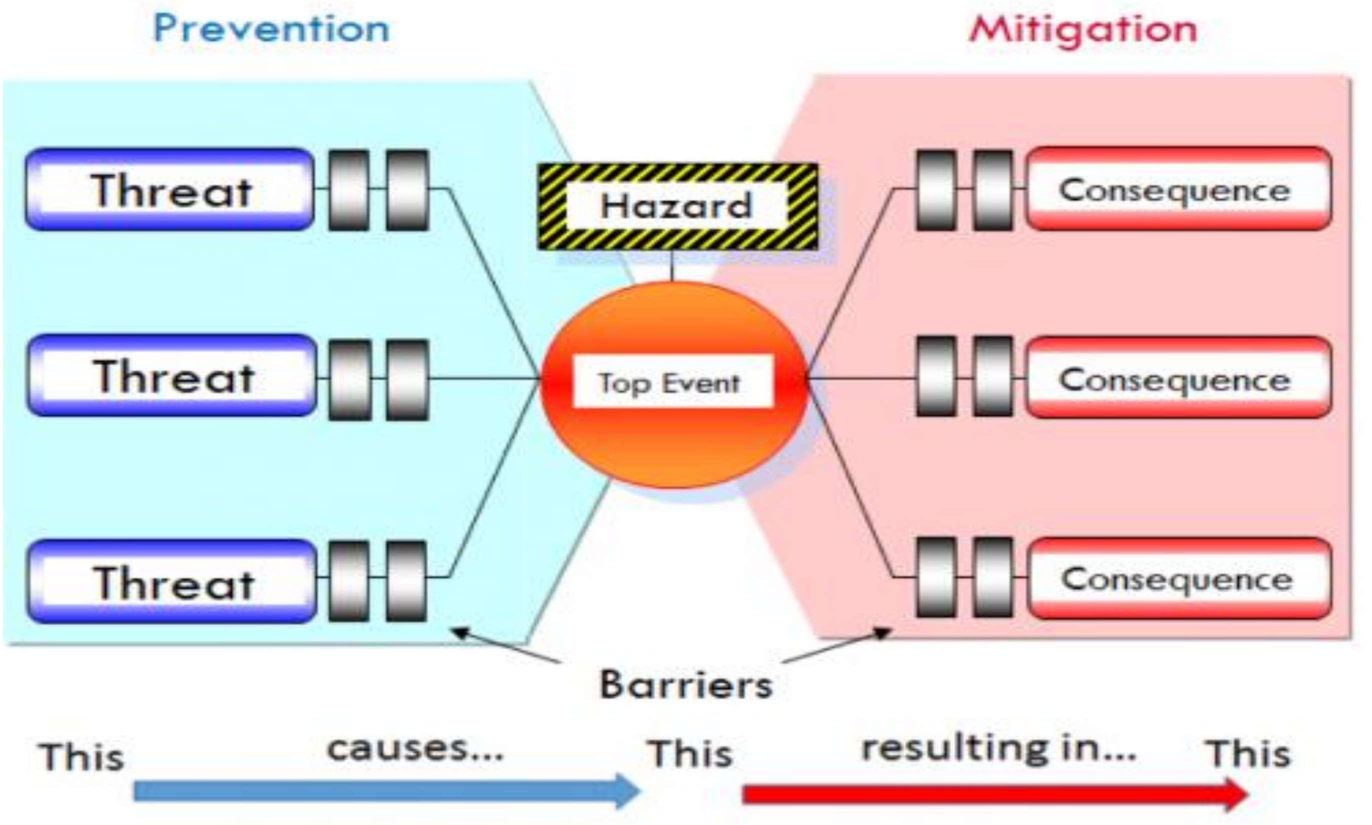
Elements of Process Safety Management

Process Safety Management (PSM)

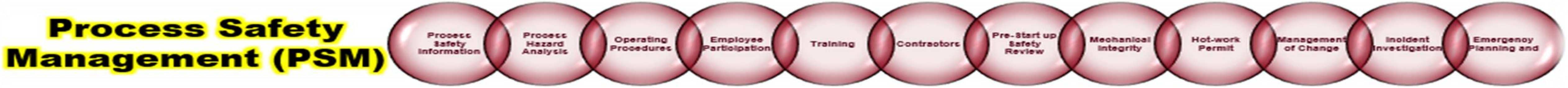
Process Safety Management in Chlor-Alkali Industry

Identification of MAH-Major Accident Hazard

PSI
PHA
OP/SP
MOC
MIQA
PSSR
Training
CSM



Incident Investigation
Emergency Planning & Response



Process Safety Management in Chlor-Alkali Industry

Process Safety Information

PSI involves collecting and maintaining detailed information on hazardous chemicals, technology, and equipment used in processes. This includes data on toxic, reactive, flammable, and explosive properties of chemicals; information on process flow diagrams, operating limits, and consequences of deviations; and equipment details like design codes, materials of construction, and relief system requirements. This data serves as the foundation for identifying hazards and assessing risks in other PSM elements.

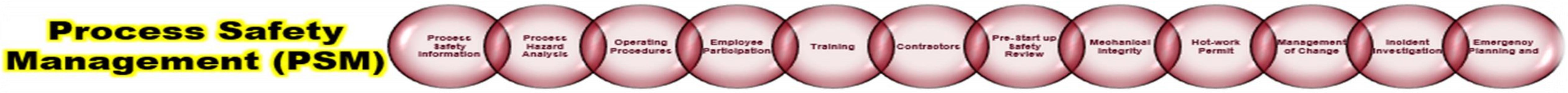
Important Notes:

- PSI must be complete, accurate, UpToDate, and accessible to users.
- Define a PSI tree/structure that must aligns with the PSI procedure for easy document retrieval.
- Use document management software or servers to store PSI documents with controlled access rights.

Process Hazard Analysis

PHA is a structured and systematic method to identify potential hazards within a process.

Common methodologies include HAZOP (Hazard and Operability Studies), What-If Analysis, and Failure Modes and Effects Analysis (FMEA). These analyses help identify and evaluate the likelihood and consequences of potential accidents, assess adequacy of controls, and recommend improvements. PHA is essential for proactive hazard identification, enabling the implementation of safety measures to prevent incidents.



Process Safety Management in Chlor-Alkali Industry

Operating Procedure

Operating procedures provide a clear understanding of parameters for safe operation for those who are operating the process.

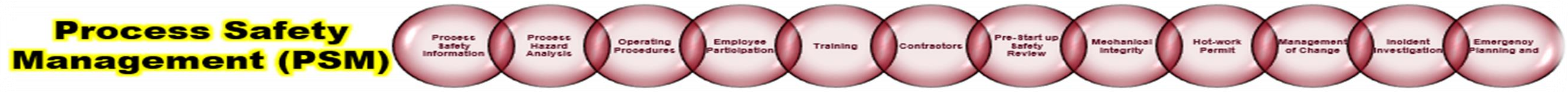
- Operating procedures also explain the safety, health, and environmental consequences of operation outside process limits.
- Safe practices provides planned system of procedures involving checks and authorizations prior to doing nonroutine work in process areas.

Management of Change

MOC is a systematic approach to managing safety risks when changes occur in processes, equipment, materials, procedures, or personnel.

The MOC process involves evaluating the impact of changes, assessing hazards, reviewing safety information, and updating procedures as needed.

MOC ensures that changes do not introduce new risks without appropriate safeguards, helping to maintain safe operation.



Process Safety Management in Chlor-Alkali Industry

Quality Assurance

Quality Assurance efforts focus on ensuring that process equipment is

- Fabricated in accordance with design specifications.
- Delivered to the proper location
- Assembled and installed properly.

Pre-Startup Safety Review

The pre-startup safety review provides a final check of new and modified equipment to confirm that all appropriate elements of process safety have been addressed satisfactorily and the facility is safe to operate.

PSSR can be done before:

a. New installations
b. After complete overhauling
c. Long shutdown

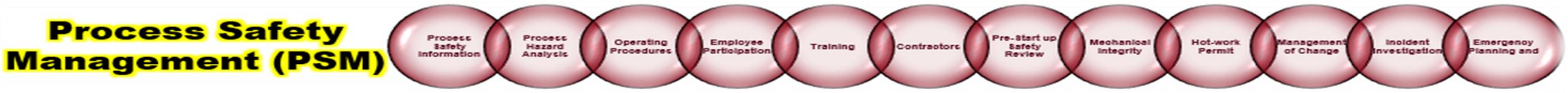
Process Safety Management in Chlor-Alkali Industry

Mechanical Integrity

MI focuses on the maintenance, inspection, and testing of critical equipment (e.g., pressure vessels, piping, relief systems, controls, and emergency shutdown systems) to ensure reliable operation and prevent equipment failure. An effective MI program includes routine inspections, preventive maintenance, and testing, along with tracking and managing equipment repairs. MI helps prevent incidents by maintaining the structural and functional integrity of equipment.

Training

Effective training programs ensure that all employees, including operators, maintenance staff, and contractors, have a thorough understanding of the process, hazards, and safety measures. Training should cover emergency response, proper use of personal protective equipment (PPE), and operating procedures. Regular refreshers, competency assessments, and specialized training for critical tasks are essential to maintain high safety standards and minimize human errors.



Process Safety Management in Chlor-Alkali Industry

Contractor Management

This element focuses on ensuring that contractors working on-site are qualified, understand the process hazards, and comply with safety policies. Contractors are often involved in maintenance, construction, or specialized tasks.

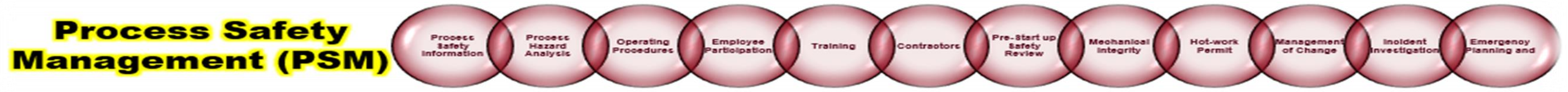
Effective contractor management includes pre-qualification, orientation on safety requirements, monitoring their adherence to safe practices, and ensuring they meet safety performance expectations.

Incident Investigation

This involves investigating any incidents or near-misses to understand root causes and contributing factors. The goal is to learn from these events and prevent recurrence.

Investigations should be thorough and timely, with findings used to develop corrective actions and improve safety systems.

Effective incident investigation supports a culture of continuous learning and improvement, addressing underlying issues to enhance overall safety.



Process Safety Management in Chlor-Alkali Industry

Emergency Response and Planning

This element ensures preparedness for emergencies, such as toxic release, fires, chemical spills, or explosions.

Emergency response plans should outline roles and responsibilities, emergency shutdown procedures, evacuation routes, communication protocols, and resources needed to mitigate impacts.

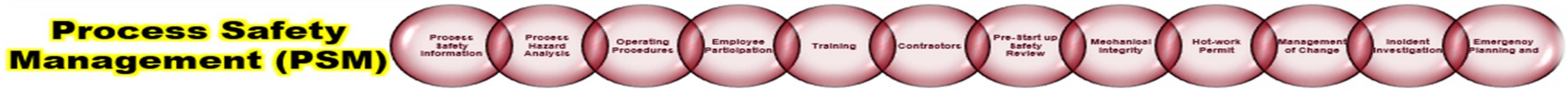
Regular drills and training ensure that employees and responders are equipped to handle emergencies effectively, minimizing harm to personnel, the environment, and assets.

Audit

Regular audits evaluate compliance with PSM standards, identifying gaps or weaknesses in safety management practices.

Audits involve reviewing records, procedures, and practices, with the goal of verifying adherence to regulations and standards. Findings are used to improve safety programs, ensuring continuous alignment with best practices and regulatory requirements.

Effective audits reinforce a commitment to ongoing safety improvements.



Hazards in Chlor-Alkali Process Industries

Three Major Hazards in Chlor-Alkali Operations:

1. Fire – Hydrogen:

- Can impact plant structures, personnel, and the environment. May also lead to secondary toxic releases.

2. Toxic Release – Chlorine Gas:

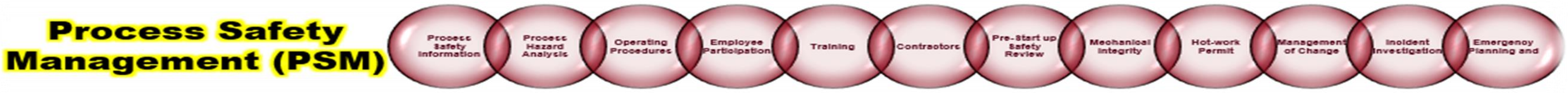
- Poses severe risks to people and the environment, with incidents like the Bhopal disaster (1984) as key examples.

3. Explosion – Nitrogen Trichloride (NCl_3) & H2 in Cl2:

- Similar to fire hazards but with more severe impact potential due to its explosive nature.

Identification of MAH-Major Accident hazard

Substance	Hazard Scenario - Consequence	Risk Ranking	MAH (Yes / No)
Low Pressure Gaseous Chlorine (0.4 barg operating pressure)	Localized Toxic Vapor Cloud	2 – Minor Injury or Health effect B2 – Low Risk	No
Medium Pressure Gaseous Chlorine (2.5-3.5 barg operating pressure)	Toxic Vapor Cloud	4 – Single Fatality or Permanent Total Disability B4 – Medium Risk (ALARP)	Yes
Liquid Chlorine	Toxic Vapor Cloud	4 – Single Fatality or Permanent Total Disability B4 – Medium Risk (ALARP)	Yes
Hydrogen	Localized Explosion in Electrolyzer	3 - Major injury of health effect A3 – Low Risk	No
NCl3 in Liq. Cl2	Toxic Vapor cloud	4 – Single Fatality or Permanent Total Disability B4 – Medium Risk (ALARP)	Yes



2. Managing MAH- Med. Pressure & Liq. Cl_2

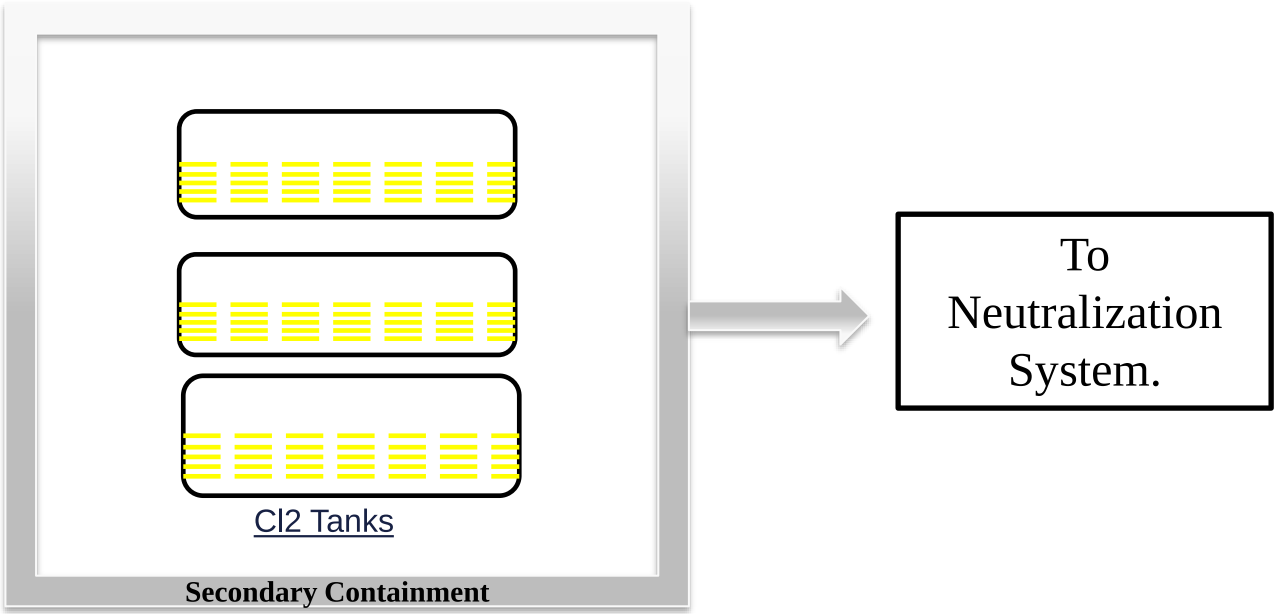
Process Safety Management In Chlor-Alkali

Managing MAH

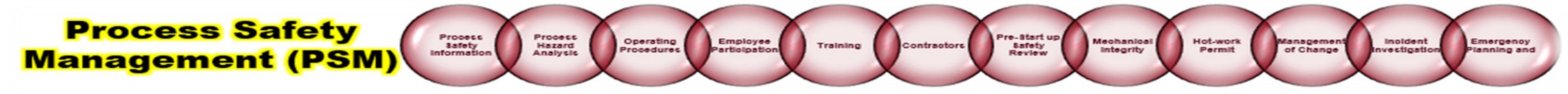
Basic HAZOP & QRA recommendations for Preventions & Mitigations of Major Accidents Events in Chlor-Alkali Industries:

1. Reduced Cl2 inventory-Consume as soon as it is produced.
2. Keep one tank empty with zero pressure as emergency standby all the time.
3. Provide secondary containment for major hazardous inventory and connection to scrubber.

Option-1
Installed in Middle East

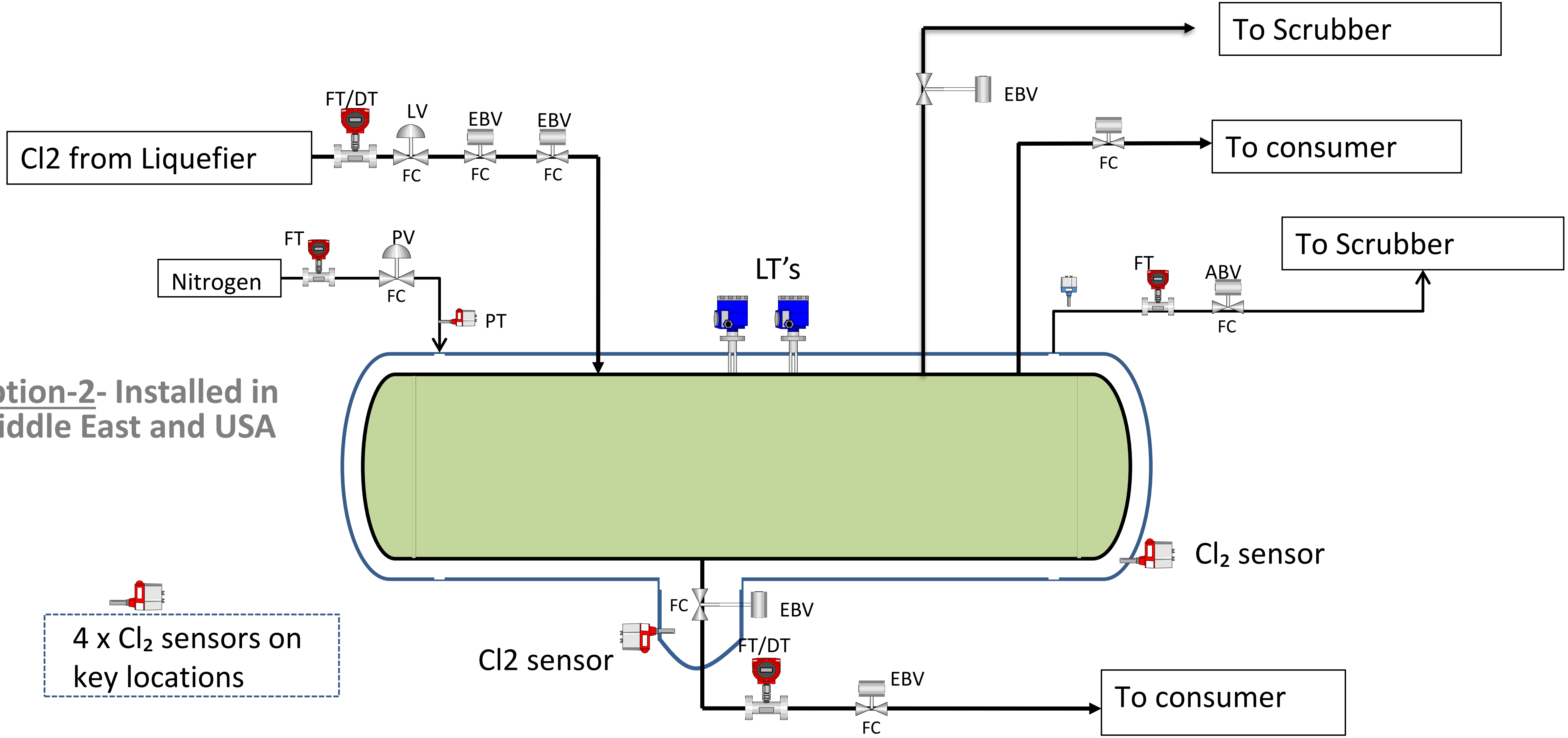


Cl2 tanks confinement

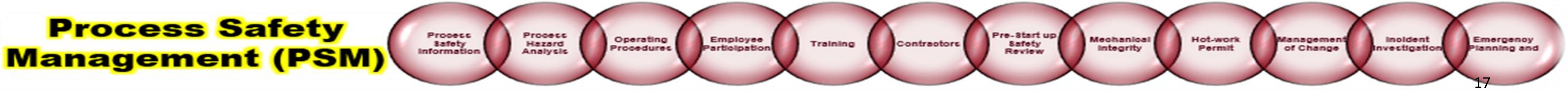


Process Safety Management In Chlor-Alkali

Managing MAH



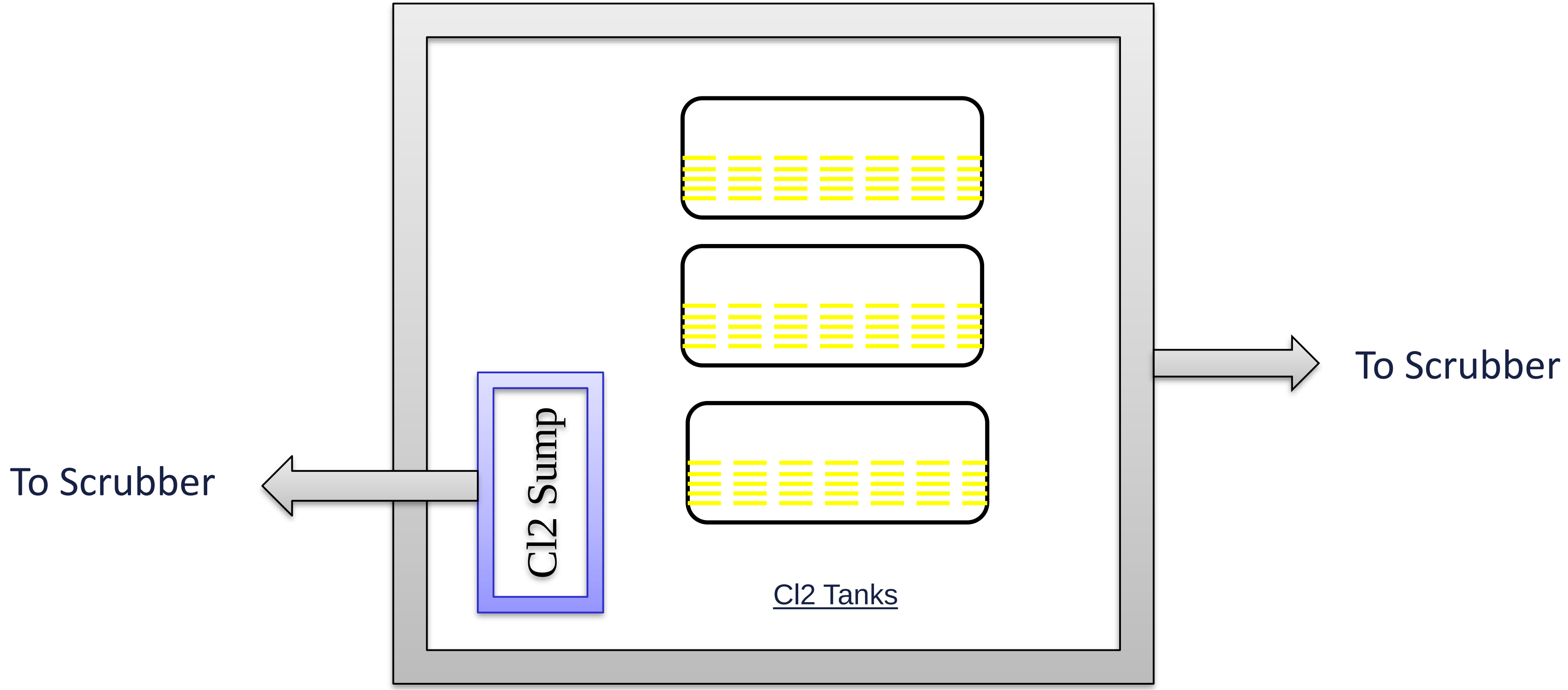
Option-2- Installed in Middle East and USA



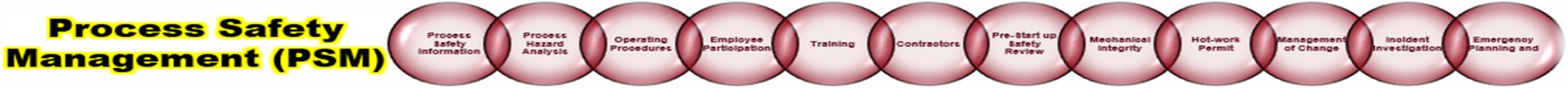
Process Safety Management In Chlor-Alkali

Managing MAH

4. Introduce Sump inside the Cl2 building connected with scrubber for major catastrophic event.



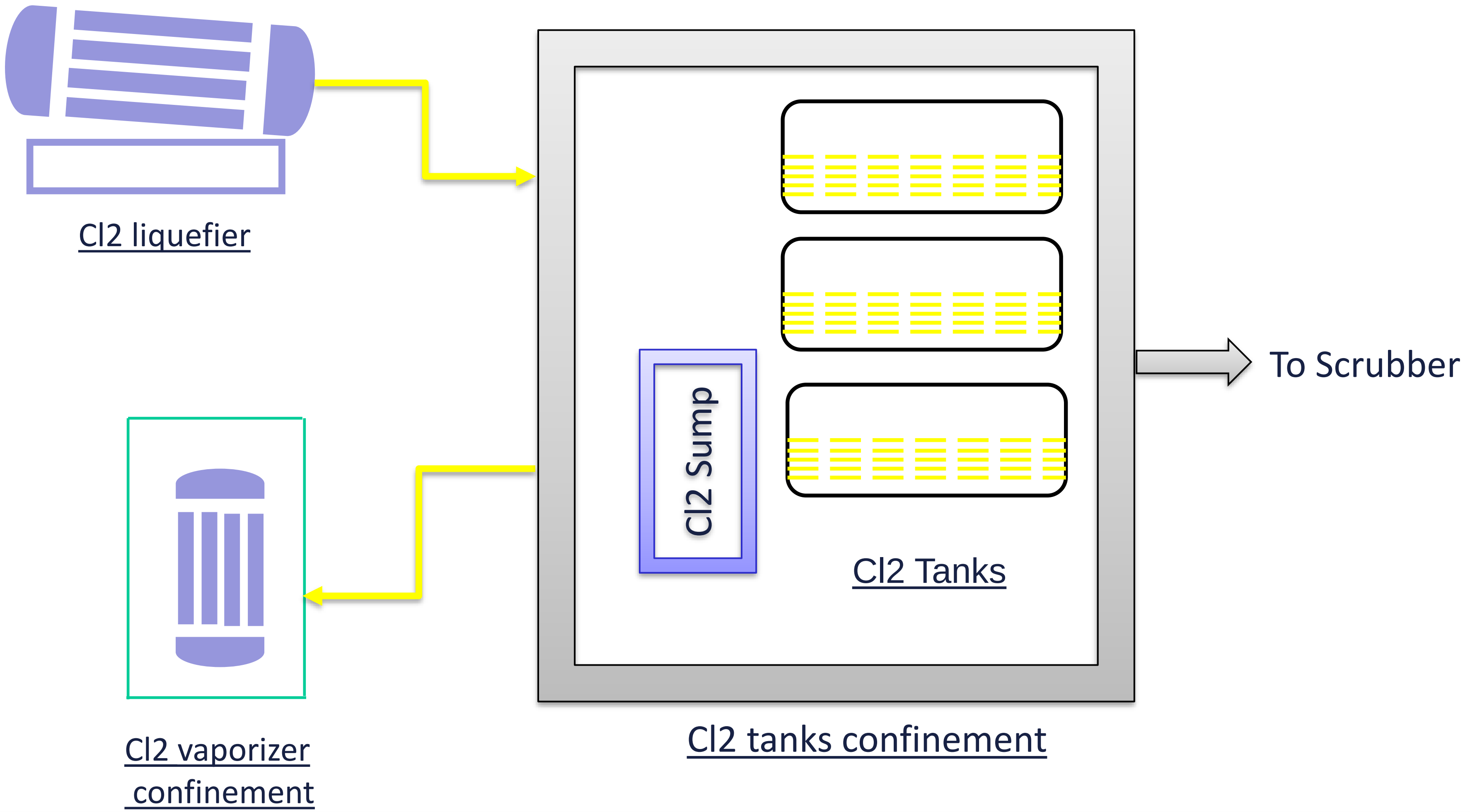
Cl2 tanks confinement

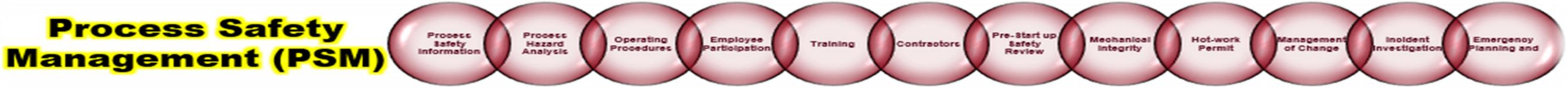


Process Safety Management In Chlor-Alkali

Managing MAH

5. Minimize the leak sources such as flanges, valves and other accessories

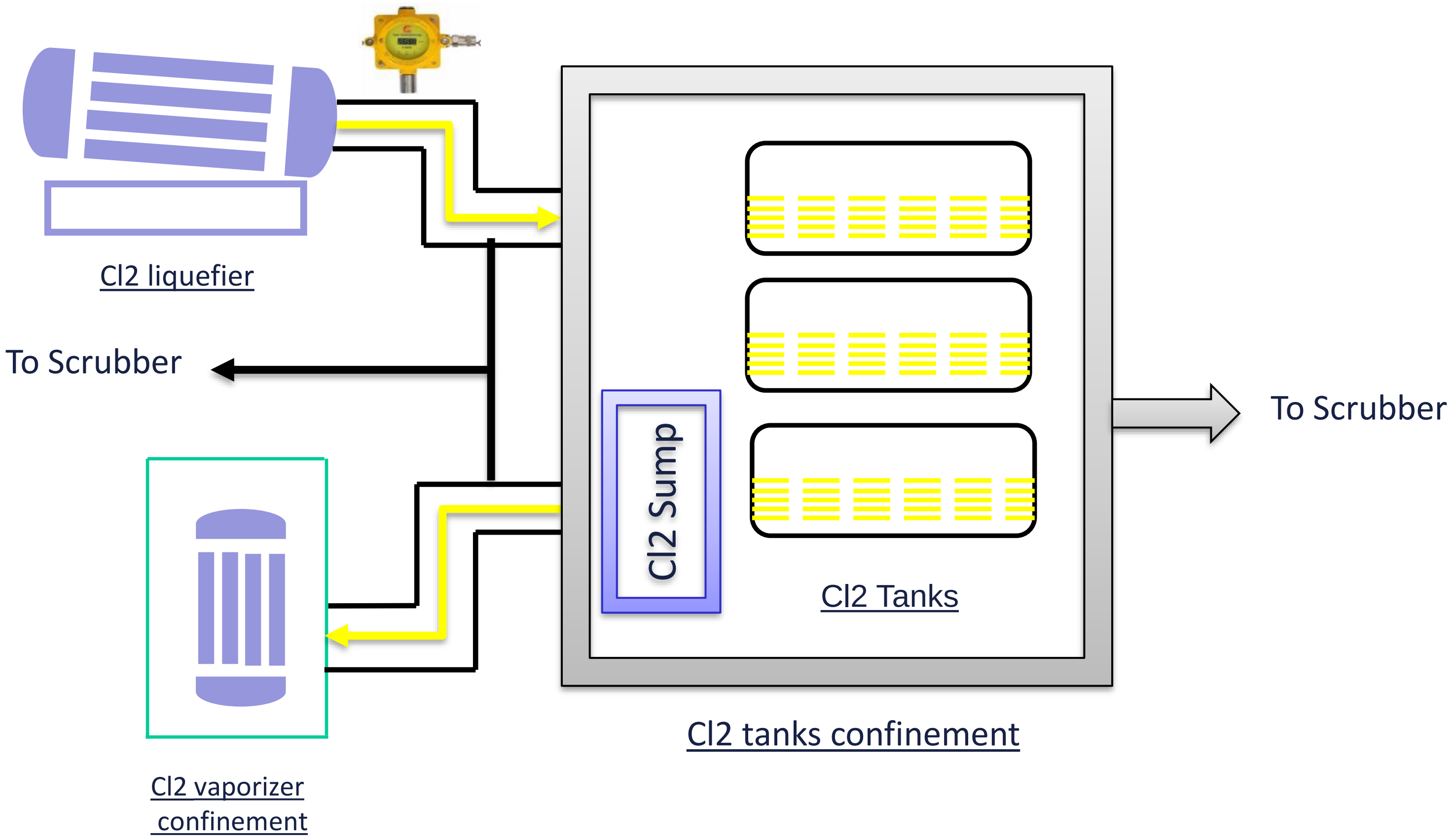


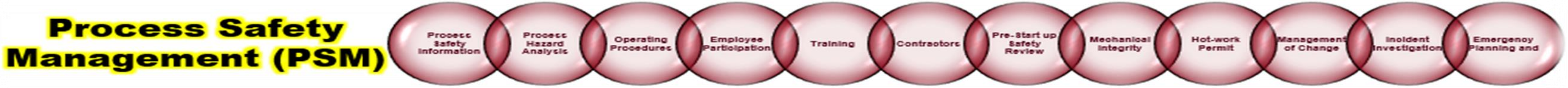


Process Safety Management In Chlor-Alkali

Managing MAH

6. Provide Secondary containment ducting for Liquid Chlorine Pipe for the Liq. Chlorine line from Cl2 liquefier to Cl2 tanks and from Cl2 tanks to Cl2 vaporizer.
The secondary containment duct should be connected with Neutralization system followed by Cl2 sensor.

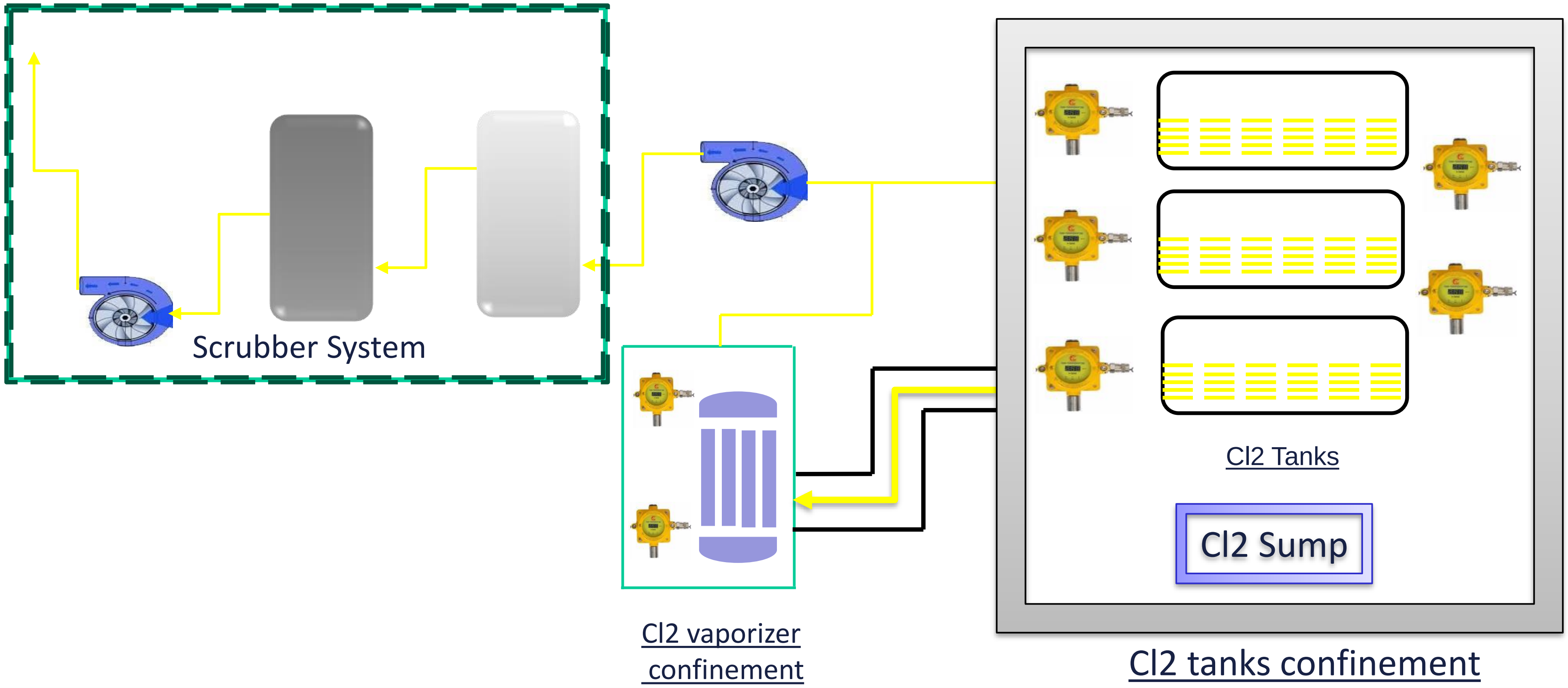


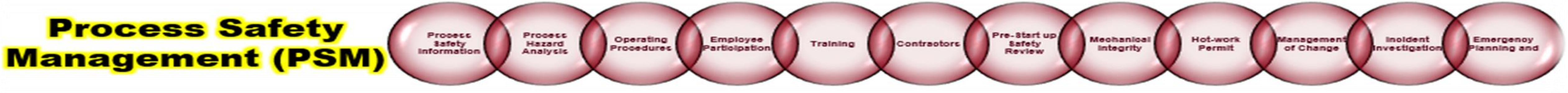


Process Safety Management In Chlor-Alkali

Managing MAH

7.Provide Emergency Blower for Degassing of Chlorine secondary containment, starts on activating chlorine sensors inside the building to evacuate chlorine to Neutralization System.

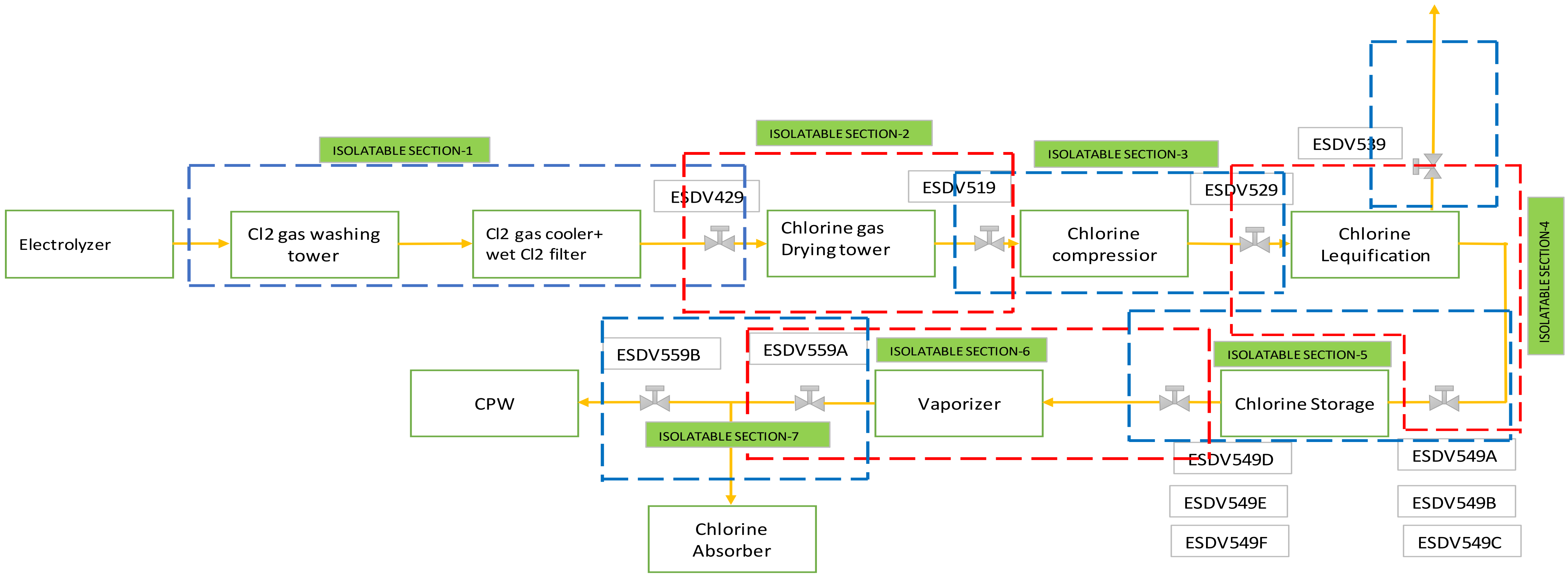


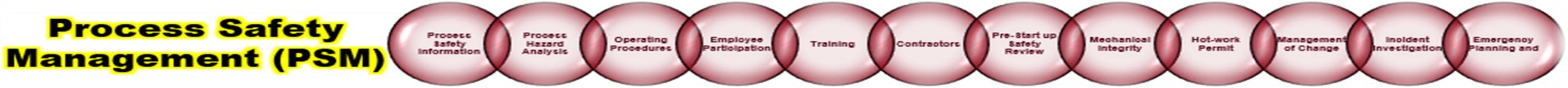


Process Safety Management In Chlor-Alkali

Managing MAH

8. Reduction of inventories by introducing Additional ESDVs.





Process Safety Management In Chlor-Alkali

Managing MAH

9. Shelter In Place

Shelter-in-Place (SIP) is a place designed to protect individuals during an unplanned release of hazardous substances, such as toxic gases or chemicals, in case evacuation is not safe or feasible. Existing facility sitting area can be used as SIP.

The below basic requirements of a standard SIP are:

a. Provide timely, reliable detection of toxic gases- Install enough Cl2 gas detectors at the facility and boundary wall.

b. Establish leak tight SIP volume to avoid any toxic gas ingression.

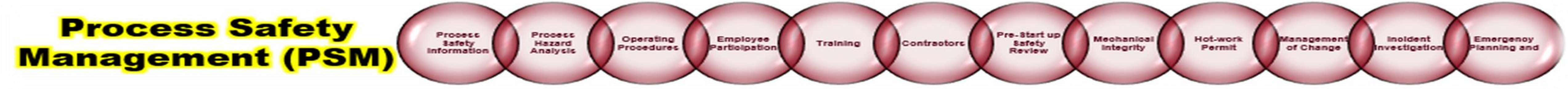
c. Provide timely, reliable isolation of ventilation systems to avoid toxic gases ingression- Provide Cl2 gas detectors at the inlet of HVAC.

d. Install an O_2 detector inside the SIP to monitor oxygen levels and provide an alternate respiratory oxygen source, such as oxygen cylinders.

e. Install reliable communication equipment for emergency updates and instructions inside the SIP.

f. Stock the SIP with essential supplies, including water, non-perishable food, and first aid kits.

g. Train personnel and provide instructions to ensure that sheltering activities are performed properly.



Process Safety Management In Chlor-Alkali

Managing MAH- Mechanical Integrity

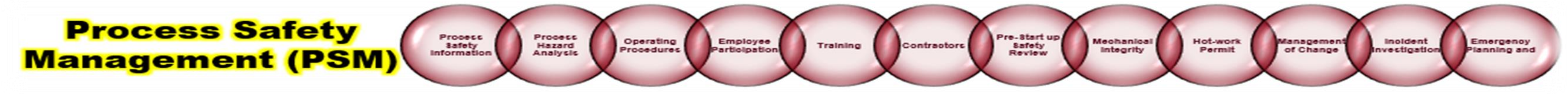
1. CUI- Corrosion Under Insulation

CUI is most common in liquid Cl2 piping and storage tanks because of its low temperature, condensation may occur.

CUI detection is challenging, as the insulation layer hides corrosion activity. However, several techniques help in identifying CUI without needing to remove all insulation:

Non-Destructive Testing (NDT) Techniques

- **Ultrasonic Testing (UT):** Measures wall thickness to detect material loss. UT is widely used but may require insulation removal at specific locations.
- **Radiography (X-Ray):** Effective for detecting corrosion and moisture under insulation.
- **Infrared Thermography:** Detects temperature variations caused by moisture under insulation. While useful, it may not always pinpoint corrosion directly.
- **Pulsed Eddy Current (PEC):** Used for inspecting corrosion in metallic materials without removing insulation. Effective for carbon steel, it measures wall thickness over a large area.



Process Safety Management In Chlor-Alkali

Managing MAH- Mechanical Integrity

Preventive Measures to Manage CUI

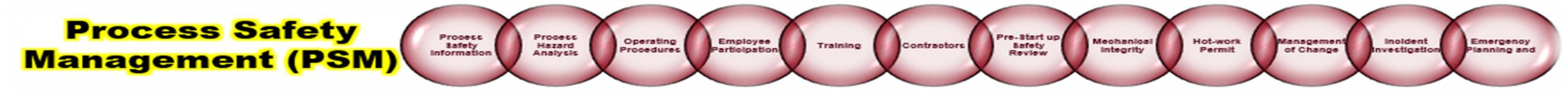
1. Improved Insulation and Cladding Selection.
2. Regular Inspections and Maintenance.
3. Temperature Control and Protective Coatings.
4. Risk-Based Inspection (RBI) and Monitoring Program.

2. Tank settlement/Subsidence Survey-(Euro Chlor GEST 87/130 Possible Hazards for Chlorine Plants and their Proposed Mitigations.)

Tank settlement monitoring is essential for ensuring the structural integrity, safety, and operational efficiency of storage tanks, which are often used in Cl2 industries for storage of Liquefied Cl2 gas. Settlement refers to the gradual sinking or shifting of a tank due to uneven ground conditions or soil compaction, which can lead to tank deformation, leaks, or even catastrophic failure if not properly managed. Recommended to conduct this survey on once in 5 years.

Techniques for Tank settlement survey:

1. Laser Scanning (LiDAR): Utilizes laser pulses to create highly accurate 3D models of the tank and its surrounding area. This helps detect any minor shifts or changes in elevation over time.



Process Safety Management In Chlor-Alkali

Managing MAH- Mechanical Integrity

2. Total Station Surveying: Measures the angles and distances from a known point to identify settlement points on the tank structure. It provides precise data on any lateral or vertical movement.

3. Differential GPS (DGPS): Offers high accuracy in detecting settlement by measuring specific points around the tank using GPS. This technique is effective for monitoring large areas.

4. Manual Levelling (Spirit Levelling): Traditional surveying technique using a levelling instrument and staff to measure subsidence across points. Although less advanced, it's cost-effective and reliable for minor settlement.

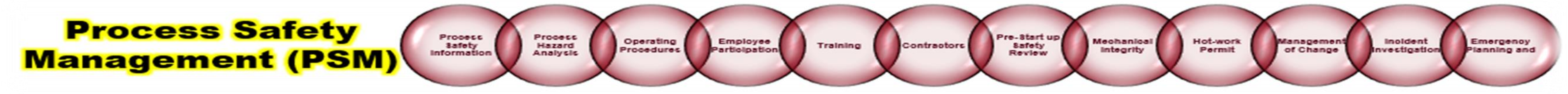
3. Pressure Safety Valve

A Pressure Safety Valve (PSV) is a crucial safety device used to protect pressurized equipment, vessels, and systems from overpressure situations, which could lead to catastrophic failure.

Consider MAH's area PSVs in Safety Critical equipment.

Use PSVs one in operation and One in Standby philosophy with one LO and another LC.

Use rapture disk on upstream of PSVs to avoid continuous contact between PSVs and operational fluid during normal operations to avoid damage of PSVs internals.



3. Managing MAH- NCl3 in Liq. Chlorine

Process Safety Management In Chlor-Alkali

Managing MAH- Past Incidents due to NCl_3

S.NO.	INCIDENT	LOCATION	DATE
1.0	One ton container exploded that was part of a Suction Chiller System	Not known	2010
2.0	Two Explosions in chlorine vaporizers have been reported, no details available	Brazil	Not Known
3.0	One-ton container exploded	Not Known	February 1949
4.0	One-ton container exploded	Not Known	November 1948
5.0	Tank car cover blew off killing two	Norway	January 1940
6.0	Three interconnected storage tanks (45 tons total capacity) at a pulp mill exploded releasing 21 tons of chlorine	Romania	December 1939
7.0	Two one-ton containers exploded	New York	July 1928

Process Safety Management In Chlor-Alkali

Managing MAH-NCl3 in Liq.Cl2

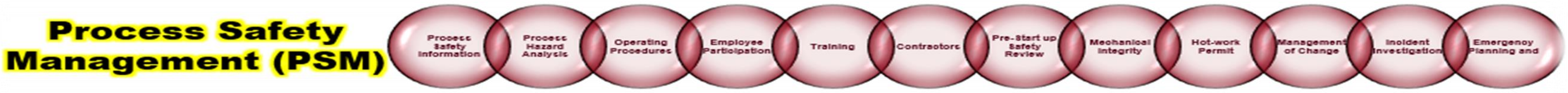
Introduction

Overview:
NCl3 is Highly Reactive and Explosive: Formed from the reaction of chlorine gas with nitrogen-containing compounds.

Properties:
Formula: NCl_3 (Trichloramine)
Physical Characteristics: Yellow, oily, pungent odor, explosive in nature
Solubility: Low soluble in water; high in chlorine, benzene, chloromethanes, carbon disulfide
Boiling Point: 71°C (Chlorine's boiling point is -34°C)

Safety Concerns:
Increased Concentration: Lower volatility than chlorine, NCl_3 concentration rises as chlorine evaporates.
Critical Threshold: At 12-13 wt% in liquid chlorine, decomposition reaction started, leading to extreme pressure increases and potential explosions (GEST 76 55 Edition 14).

Note:
It's important to note that under normal operating conditions in current chlor-alkali production facilities, nitrogen gas introduced into the chlorine stream does not convert into nitrogen trichloride **(as referenced in Cl2 Institute Pamphlet 152, 4.1.3).**



Process Safety Management In Chlor-Alkali

Managing MAH- Source of Contamination

Mined Salt/Water Sources

Ammonia contamination can come from impurities in mining water or natural nitrogen compounds in solid salt.

Groundwater Use

Groundwater can leach ammonia compounds and humic acid from fertilized fields into brine wells.

01

02

03

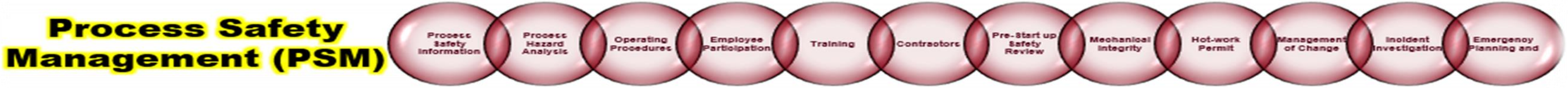
04

Rock Salt Usage

The mining of rock salt often involves the use of explosives, which may contain nitrogen compounds.

Vacuum salt usage

The use of vacuum salt in brine recycled circuits tend to give very low levels of NCl3, however ferrocyanide anti-caking agents can introduce nitrogen to the salt



Process Safety Management In Chlor-Alkali

Managing MAH- Process of Formation in Chlor-Alkali

Primary Formation Conditions:

Electrolyzers Anodic Cells: Anolyte in electrolyzers with pH < 5 facilitates rapid NCl_3 production in the presence of ammonia/ammonia compounds in Brine.

(Ideal environment for NCl_3 formation due to favorable pH and process conditions)

Key Reactions

1. $NH_3 + 3\ Cl_2 \rightarrow NCl_3 + 3\ H^+ + 3\ Cl^-$
2. $NH_4^+ + 3\ Cl_2 \rightarrow NCl_3 + 4\ H^+ + 3\ Cl^-$
3. $NH_4^+ + Cl^- + 3\ HClO \rightarrow NCl_3 + H^+ + Cl^- + 3\ H_2O$

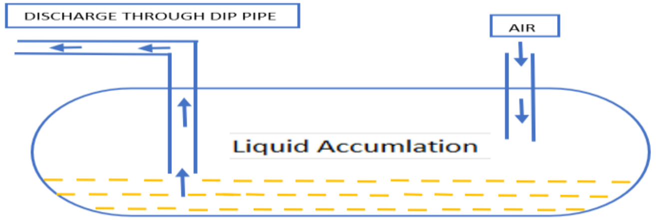
(Reference: Cl_2 Institute Pamphlet 152, Section 4.2)

Process Safety Management In Chlor-Alkali

Managing MAH- Possibility of NCl_3 accumulation in Cl_2 system

a. Chlorine Storage Vessels:

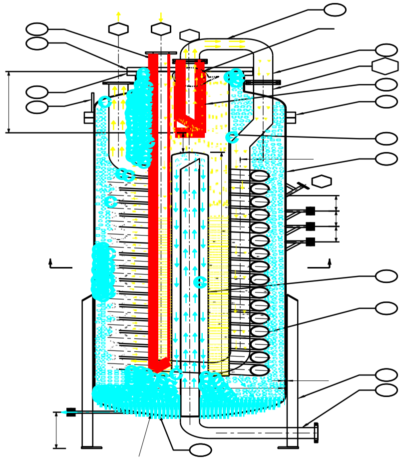
Chlorine storage tanks are the key area where NCl3 can be accumulated at the bottom of the tank when Liq. Cl2 is drawn from top of the tank during the process. NCl3 gets settled down in tank bottom because of its higher density and can get accumulated and enrich its concentration over a time period.



b. Chlorine Evaporators/Vaporizers - Design and Operation:

Vaporizers are the second key area where NCl3 can accumulate.

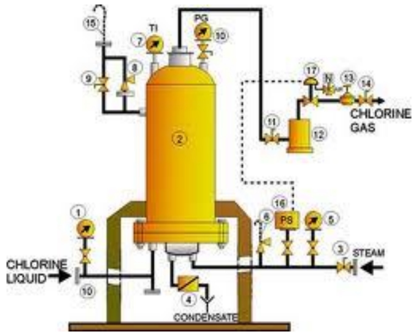
Vaporizers can be categorized based on their design. For our purposes, they fall typically into three categories as follows:



i) Plug Flow Vaporizers: These include coil-in-bath, vertical tube vaporizers, or rising film evaporators. Chlorine passes through the vaporizer linearly as a slug, progressively boiling during its passage. There is no recirculation or remixing of the chlorine with fresh chlorine entering the vaporizer. The operating temperature of such type of vaporizer is also high.

Process Safety Management In Chlor-Alkali

Managing MAH- Possibility of NCl3 accumulation in Cl2 system



ii) **Constant Volume Vaporizers:** These typically have a heating device inside, such as a kettle vaporizer or bayonet vaporizer. Liquid chlorine is added to the vessel where it is boiled, and the vaporized gas is removed.
Constant volume vaporizers maintain a pool of liquid chlorine. In these vaporizers, liquid chlorine containing nitrogen trichloride is added to the pool, and chlorine gas with relatively little nitrogen trichloride is removed, leading to NCl3 accumulation in the liquid chlorine pool until equilibrium is reached. **(Reference: GEST 76 55 Edition 14 - Section 5.5)**

iii) Low-Temperature Vaporizer/Hot Water Bath in Vaporizer:

Avoid using low-temperature vaporizers or vaporizers operating with hot water. They are operated at low temperatures.

Operate the vaporizers at temperatures above 50-70°C (as in plug flow vaporizers or distillation units) can result in the destruction of some NCl3.

(Reference: GEST 76 55 Edition 14 - Section 7.2)

c. Accumulation of NCl3 in Dead Ends of Cl2 Tanks and Vaporizers and its connecting pipes.

Process Safety Management In Chlor-Alkali

Managing MAH- Managing NCl_3 explosion risk

<u>Preventive Control:</u>

a. Raw Material Sourcing:

Preventing nitrogen trichloride formation primarily involves keeping ammonia compounds away from the process.

Consider the following general principles:

- Use sea salt.
- Avoid Rock salt- Rock salt may be mined by using nitrogen-based blasting compounds

(Reference: GEST 76 55 Edition 14 - Section 8.1)

b. Periodic Monitoring of Ammonium Compounds in Salt and Brine:

Analyse nitrogen compounds in the brine periodically to predict resulting NCl_3 concentrations in liquid chlorine.

(Reference: GEST 76 55 Edition 14 - Section 8.1)

Component	Raw Brine (Salt)	Treated Brine	Purified Brine
Nitrogen Compounds	0.1- 3 PPM NH_3	< 100 PPB NH_3	< 100 PPB NH_3

Process Safety Management In Chlor-Alkali

Managing MAH- Managing NCl3 explosion risk

c. Water Analysis:

Conduct water analysis to check for ammonia content.

d. NCl3 Monitoring in Chlorine:

Analyse NCl3 concentration in liquid chlorine and chlorine gas after the drying tower. This continuous measurement provides direct indications of NCl3 levels. (Reference: GEST 76 55 Edition 14 - Section 8.2)

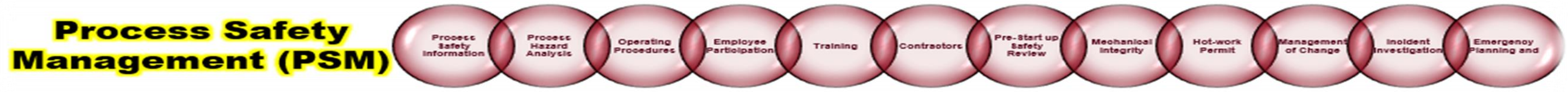
Note- The maximum admissible concentration of NCl3 in liquid chlorine in production, storage, transport or use should be less than 20 mg/kg. (Reference: GEST 76 55 Edition 14 - Section 6.0)

Techniques for Detection:

- Spectroscopic methods, gas chromatography, and colorimetric analysis.

Safety Monitoring Systems:

- Real-time NCl_3 monitoring in production lines.



Process Safety Management In Chlor-Alkali

Managing MAH- Managing NCl3 explosion risk

<u>**Engineering Controls**</u>

a.- Design of Tanks: Inherent Safe Design

Ensure Chlorine Discharge from the Lowest Point in the Tank, if bottom discharge is available. This Eliminates any possibility of NCl3 accumulation.

b. Vaporizer for Cl2 Service - Design and Operation:

Review vaporizer and reboiler designs to minimize NCl3 accumulation. (Reference: Cl2 Institute Pamphlet 152, Section 8.5)

c. Avoid Dead Ends in Pipelines:

Prevent the dead ends in Liq. Cl2 piping's to avoid accumulation of NCl3.

Critical Inferences provided in Euro Chlor GEST/Cl2 institute pamphlet.

a. NCl3 is denser than liquid Cl2, causing it to settle at the bottom of the Cl2 tank and exit first during tank bottom discharge.
b. Under normal operating conditions, nitrogen gas does not react with Cl2 to form NCl3 (Reference: Cl2 Institute Pamphlet 152, 4.1.3).

Thank You