FM Property Loss Prevention Data Sheets 7-111E

October 2020
Interim Revision April 2026
Page 1 of 12

CHLOR-ALKALI

Table of Contents

List of Figures

1.0 SCOPE

This document provides recommendations for the prevention of and protection against fire and explosions in electrolytic chlorine processing facilities. The predominate methods to produce chlorine (Cl_2), hydrogen (H_2) and caustic (NaOH) is electrolysis of saturated brine (NaCl solution) in membrane or diaphragm cells with capacity commonly based on ECUs (electrolytic chlorine units). Other saturated brine solutions can be substituted for NaCl solutions.

Due to the retirement of mercury cell technology, the hazards of mercury cells are not considered in this document.

1.1 Hazards

The production process involves flammable gasses, chemical reactivity hazards that can result in explosions, large electrical installations, rotating equipment, and plastics in construction. The occupancy is inherently corrosive. In addition, the process generates hydrogen, which can be used as supplemental fuel for boilers, gas-turbine generators, vented, burned to make HCl, or sold. Caustic concentration requires evaporators and circulation pumps of special alloy (nickel) metal construction with a large steam demand. The loss drivers in the occupancy are explosions in the chlorine gas and hydrogen gas headers, the potential formation of nitrogen trichloride (NCl_3) in liquid chlorine, fires in chlorine compressors or faults in large transformers, interruption of power from on-site/off-site power-generation units, rotating equipment failures, and fires in plastic construction.

1.2 Changes

April 2026. Interim revision. The following changes were made:

A. Deleted Section 3.2.2.4 for partial solutions for inferential monitoring systems and created Section 3.2.3 for cell monitoring systems.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

The recommendations in this document address human errors, equipment malfunctions, and process safety that may lead to process equipment explosions, fires, and/or damage in electrolytic chlorine plants.

2.2 Construction and Location

2.2.1 Transformers

2.2.1.1 Provide adequate separation or barriers between transformers and buildings and groups of transformers in accordance with Data Sheet 5-4, *Transformers*.

2.2.2 Cell Buildings

2.2.2.1 Provide noncombustible and corrosion-resistant steel support system for cell buildings.

2.2.2.2 Provide noncombustible wall panels or FM Approved FRP panels for cell buildings. If plastic construction materials are used, see Data Sheet 1-57, *Plastics in Construction*, for additional information and guidance.

2.2.2.3 Provide natural ridge ventilation inside cell buildings and other buildings where a release of hydrogen gas could occur. If natural ventilation is not provided, then provide a means to detect hydrogen concentration interlocked to automatic ventilation.

2.2.3 Ductwork

2.2.3.1 Install FRP ductwork moving process gases so they are not exposed to potential fires from buildings, transformers, lubrication oil, or other equipment.

2.2.3.2 Arrange combustible ductwork and headers in cell buildings in a way that ductwork congested areas are prevented. If this arrangement is not possible or practical, install fire-retardant or noncombustible ductwork.

2.2.4 Piping Systems

2.2.4.1 For piping in wet or dry chlorine streams, use noncombustible construction materials that have been proved suitable for the operation. Titanium can be used in wet-chlorine streams but not in dry-chlorine streams due to the high reactivity between them. If combustible piping construction materials such as FRP, dual laminates with chlorinated polyvinyl chloride (CPVC) liners, polytetrafluoroethylene (PTFE), etc. are used, consider that combustible piping materials will introduce additional combustible loading.

2.2.4.2 Locate carbon steel piping carrying dry product chlorine (Cl_2) gases away from any fire exposures.

2.2.4.3 Minimize exposure of gaseous chlorine (Cl_2) and hydrogen piping to fires from lubrication oil near chlorine compressors and outdoor oil-filled transformers.

2.2.5 Ensure appropriate materials are used for the construction of equipment (pumps, evaporators, storage tanks, etc.) and piping handling or processing sodium hydroxide solutions.

2.3 Process Safety

2.3.1 Establish a formal process safety program in accordance with Data Sheet 7-43, *Process Safety*.

2.4 Protection

2.4.1 General

2.4.1.1 Provide fire protection for transformers in accordance with Data Sheet 5-4, *Transformers*.

2.4.1.2 Provide automatic sprinkler protection for compressors with steam turbine drivers in accordance with Data Sheets 7-95, *Compressors*, and 7-101, *Fire Protection for Steam Turbines and Electric Generators*.

2.4.1.3 Provide fire protection for FRP cable trays according to Data Sheet 5-31, *Cables and Bus Bars*.

2.4.2 Indoor Fire Protection

2.4.2.1 For areas where combustible building constructions are present, provide protection in accordance with Data Sheet 1-57, *Plastics in Construction*, or replace it with noncombustible construction. For protection inside buildings where corrosive atmospheres can be expected, use stainless steel piping and sprinklers.

2.4.2.2 For noncombustible building construction and where a concentration of plastic ductwork, tanks, drying towers, scrubbers and equipment exists typically adjacent to and downstream of the diaphragm and membrane cell production equipment, provide protection over the area of concentration of plastic materials in accordance with Data Sheet 7-78, *Industrial Exhaust Systems*, or Data Sheet 3-26, *Fire Protection for Non-Storage Occupancies*, using Hazard Category HC-3.

2.4.3 Outdoor Fire Protection

2.4.3.1 Provide directional water spray protection for important plastic equipment and ductwork located outdoors according to Data Sheet 7-78, *Industrial Exhaust Systems*. Focus on concentrations where large ducts cross over each other or multiple vessels are positioned side-by-side. Design the system to provide a discharge pressure of 20 psi (1.4 bar) for open sprinklers or nozzles greater than or equal to 1/2 in. (13mm) or 30 psi (2.1 bar) for smaller nozzles.

For very large duct and vessel systems outdoors (e.g. scrubbers, drying towers, etc.) use of automatically controlled monitor nozzles or manual protection with a suitable fire brigade, may provide equivalent protection to fixed water spray systems.

2.4.3.2 Institute a policy that ordinary combustibles are not to be staged or stored below long run ducts.

2.5 Equipment and Processes

2.5.1 Dilution Safeguard Systems (DSS)

2.5.1.1 Provide chlorine streams with dilution safeguard systems (DSS) to prevent the formation of explosive concentrations of hydrogen (see Figure 3.2.2.1). For the correct design, selection, and operation of the DSS, consider all the following:

A. Perform a PHA to identify all the points where a process upset could be expected. Consider plant experience, industry practices, and the likelihood and potential consequences of an explosion.

B. Establish the appropriate monitoring frequency and settings for alarm and trip points based on the process upsets identified in the PHA. Allow adequate response time for operators to intervene and prevent the formation of an explosive atmosphere.

C. Ensure safety interlocks are supervised, hard-wired, and independent of the process operating controls.

See Section 3.2.2.1 and Appendix A for additional information.

2.5.2 Hydrogen Monitoring Systems

2.5.2.1 Install continuous hydrogen monitoring systems on the wet chlorine gas header prior to drying towers or other downstream units. Set the alarm and trip points considering a safety factor below the explosive range. A rate-of-change alarm for hydrogen concentration can provide an additional safeguard.

The alarm set point should not exceed hydrogen concentration greater than 2% and the trip circuit set point should not exceed hydrogen concentration greater than 3%.

2.5.2.2 Install hydrogen monitoring systems in the dry chlorine gas header prior to Cl_2 compression and liquefaction to keep the hydrogen concentration in the chlorine header below 5%. Alarm points are exceeded typically around 4%. Add dilution air (DSS) or an inert gas to the chlorine steam prior to the first stage of liquefiers (see Figure 3.2.2.1).

2.5.2.3 Install hydrogen monitoring systems in the dry chlorine gas header after liquefaction in the tail gas stream to keep the hydrogen concentration in the chlorine header below 6%. Alarm points are exceeded typically around 5%. Add dilution air (DSS) or an inert gas to the chlorine steam prior to the first stage of liquefiers (see Figure 3.2.2.1).

2.5.2.4 In the event of a circuit trip due to high hydrogen (H_2) in chlorine (Cl_2) header, purge and divert in a safe manner the H_2 and Cl_2 headers. See Section 2.6.1.2 for additional information.

2.5.3 Cells Monitoring Systems

2.5.3.1 Provide voltage monitoring of individual cells to detect when breakthrough of a membrane cell or diaphragm cell occurs.

At diaphragm cell locations, voltage monitoring may be done on a group of cells rather than individual cells. This can be done manually or by installing a group of cells and monitoring continuously.

2.5.3.2 In membrane cells, provide pressure differential interlocks between the cathode and the anode to keep the membrane tight against the screen and to prevent tearing of the membrane. In addition, provide catholyte and anolyte flow sensors to keep the membrane fully submerged.

2.5.3.3 Provide high-temperature interlocks on membrane circuits interlocked to shut off circuit power. This is a secondary means to detect the loss of brine flow.

2.5.3.4 Install alarms to monitor the liquid levels of the cells (membrane and diaphragm). Monitor for low levels and set the alarms to allow operators enough time to respond and make flow adjustments to keep levels adequate.

2.5.3.5 Provide automatic power shutdown of the cells upon sprinkler activation.

2.5.4 Chlorine Compressors

2.5.4.1 Provide thermal detection of chlorine gas entering and exiting the chlorine compressors. Provide interlocks to shut down the compressor at a minimum of 50°F (30°C) below the ignition temperature of chlorine in steel piping.

For additional guidance, refer to Data Sheet 7-95, *Compressors*.

2.5.5 Hydrogen and Chlorine Headers

2.5.5.1 Install flash-back protection on the hydrogen header shortly after the hydrogen cell headers join together.

2.5.5.2 Where water seals are used as flash-back protection on the hydrogen header, install level detection on the water seal. Provide alarms for low level and an interlock to trip the cells if a low-low level condition arises.

2.5.5.3 Provide adequate overpressure protection for the chlorine header to prevent back pressure on the membrane cells. Direct the venting to a safe location, typically to the emergency scrubber.

2.5.5.4 Provide systems to decompose nitrogen trichloride (NCl_3) in chlorine headers or areas where (NCl_3) can accumulate if high levels of ammonia and other nitrogen-containing compounds in raw brine are unavoidable (see also 2.6.1.1).

2.5.6 Design heat exchangers located after chlorine drying towers to have a higher chlorine pressure than the cooling water pressure. Provide a means to detect a tube leak with conductivity monitoring or other appropriate methods.

2.5.7 Provide transformers and rectifying transformers with protective interlocks and condition monitoring as specified in Data Sheet 5-4, *Transformers*.

2.5.8 For steam turbine generators (STGs), refer to Data Sheet 13-3, *Steam Turbines*.

2.5.9 For boilers, refer to Data Sheets 6-4, *Oil and Gas-Fired Single-Burner Boilers*, and 6-5, *Oil and Gas-Fired Multiple Burner Boilers*.

2.5.10 Provide positive pressure and/or carbon filters on intake air or damper isolation w/HVAC shutdown to mitigate the potential for chlorine gas to enter the control room. Air intakes should be elevated. SCBA and permanent breathing air supply for board operators may be warranted depending on arrangement of the control room.

2.6 Operation and Maintenance

2.6.1 Normal Operation

2.6.1.1 Establish quality controls to limit the concentration of ammonia and other nitrogen-containing compounds that can promote formation of NCl_3 (e.g., incoming rock salt, other sources of brine). Where high levels of ammonia in raw brine are unavoidable, install an ammonia destruction step in the brine treatment process (see 2.5.5.4).

2.6.1.1.1 Conduct regular testing to determine if any formation of NCl_3 is occurring within the plant.

2.6.1.1.2 Establish quality controls to limit the use of additive chemicals and process water that may introduce ammonia or other nitrogen-based chemicals.

2.6.1.2 Provide purge gas systems and establish procedures for purging equipment, piping, and headers where hydrogen explosion hazards are present, including during normal startup and shutdown, process upsets, emergency shutdown, and restart after an emergency shutdown.

2.6.1.2.1 Document all procedures and establish frequencies for routine sampling and measurement of hydrogen, oxygen, chlorine, and NCl_3 concentrations in all gaseous headers, liquid streams, liquid storage vessels, and equipment subject to explosion hazards.

2.6.1.2.2 Maintain records of the results to trend the H_2 concentration in chlorine streams.

2.6.2 Emergency Procedures

2.6.2.1 Provide documented emergency procedures for operator response to abnormal conditions such as loss of power, brine flow, steam, instrument air, water, DSS, or other critical services including process upsets and equipment failures.

2.6.2.2 Provide an emergency brine flow system or emergency procedures to keep diaphragm cells flooded.

2.6.2.3 Establish a formal power isolation plan for the whole cell building, to deenergize all electrical power to the electrolyzers, except power to lighting, in the event of an emergency.

2.6.2.4 Document the alarm and trip points and emergency response plan for all process deviations that could lead to a need for trip of the cells or downstream equipment to prevent explosions, as identified in the PHA.

2.6.2.5 Establish a documented procedure and pre-start checklist for restarting after an emergency shutdown.

2.6.2.6 Conduct periodic table-top drills with operators to practice emergency response procedures. See Data Sheet 10-8, *Operators*, for additional information.

2.6.3 Maintenance

2.6.3.1 Establish an asset integrity monitoring program in accordance with Data Sheet 9-0, *Asset Integrity*.

2.6.3.2 Perform and document regular maintenance, testing, and inspections on instrumentation and safety interlock systems related to the prevention of explosions. For additional information see Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks* (SCAI).

2.6.3.3 Perform regular recorded calibrations of hydrogen (H_2) detection equipment (in Cl_2 streams) in accordance with the manufacturer's instructions and plant experience.

2.6.3.4 When hydrogen monitoring equipment is taken out of service, follow an established bypass interlock management system to ensure the equipment is placed back in service as soon as possible.

2.7 Utilities

2.7.1 Provide FM Approved combustion control logic systems and equipment for burners where high purity hydrochloric acid (HCl) is produced.

2.7.2 Follow the protection guidelines in Data Sheet 6-13, *Waste Fuel-Fired Facilities*, where hydrogen is sent to utilities for steam production and power generation.

2.7.3 Provide backup emergency power for the emergency chlorine scrubber liquid circulation system and blower.

2.7.4 Provide a sufficient and automatic backup uninterruptible power for the chlorine header emergency scrubber, to be able to operate the scrubber during a major power outage.

2.8 Contingency Planning

2.8.1 Equipment Breakdown Spares

2.8.1.1 Equipment breakdown spares for chlor-alkali processes are intended to be used in the event of an unplanned outage of chlorine process equipment to reduce downtime and restore operations. Provide the following equipment breakdown spares as full spares:

A. Chlorine compressor

B. Rectifier transformer

2.8.1.2 Use an N+1 approach for the rectifier transformer equipment breakdown spare, so the transformer can be put directly into service.

2.8.1.3 Maintain the chlorine compressor and rectifier transformer equipment breakdown spare viability per Data Sheet 9-0.

2.9 Electrical

2.9.1 Provide electrical equipment with a Class I, Division 2 electrical classification in areas with the potential for hydrogen release or accumulation points.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

FM losses in this occupancy from 2009 to 2018 are presented in Figure 3.1, where the three largest categories of loss by peril were explosion, electrical breakdown, and fire.

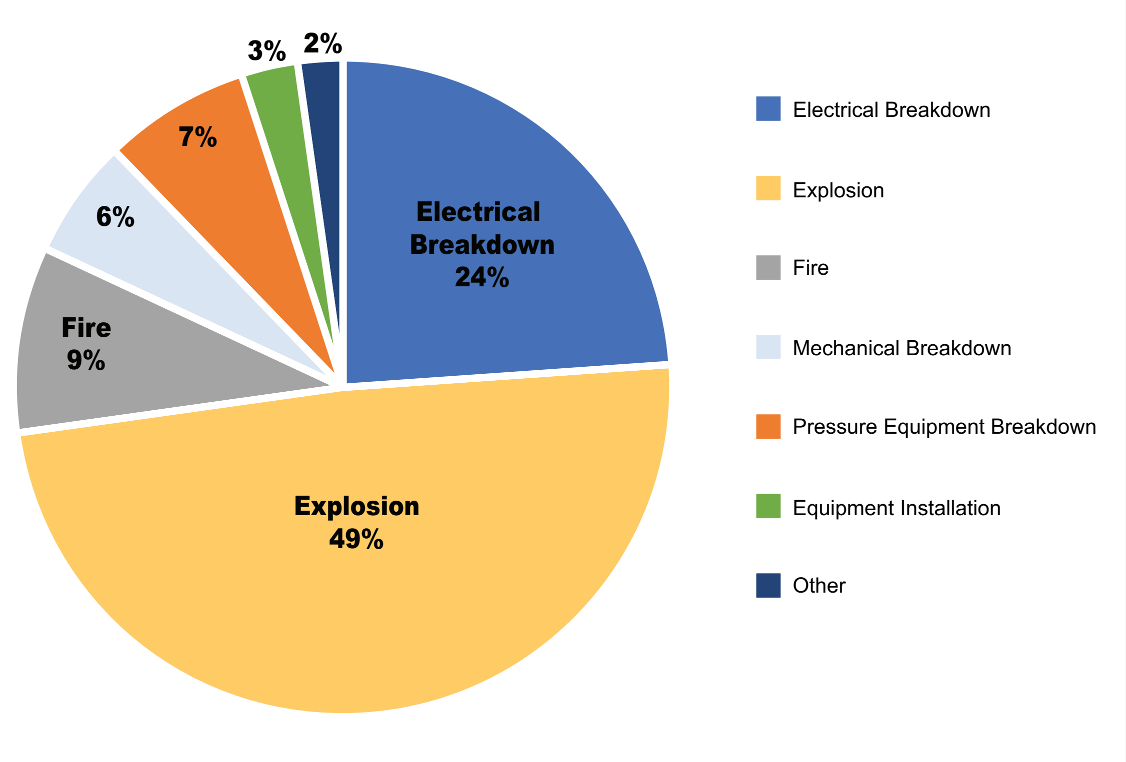

Fig. 3.1. Losses by peril, 2009 to 2018

One of the largest explosion losses occurred when an explosive mixture of hydrogen in chlorine, in the tail gas exiting secondary liquefaction, was ignited by an unidentified source. Several equipment and piping sections were damaged, impeding operations for several weeks.

Another hydrogen explosion occurred during testing of the cells and resulted in damage to over 100 membrane cells. The explosion originated as a result of a leak in a valve that was isolating the electrolyzer from the hydrogen header.

The largest electrical breakdowns in this occupancy were mostly related to transformer damage and turbine generator overspeed damage.

3.2 Process Overview

Chlorine (Cl_2), hydrogen (H_2), and sodium hydroxide or caustic soda (NaOH) are produced by electrolysis of a treated brine solution, being the most common sodium chloride (NaCl), as shown in the following electrolysis chemical equation:

$$2\ \mathrm{NaCl(aq)} + 2\mathrm{H_2O} \rightarrow \underbrace{\mathrm{Cl_2(gas)}}_{\text{Anode}} + \underbrace{\mathrm{H_2(gas)} + 2\mathrm{NaOH\ (aq)}}_{\text{Cathode}}$$

Large electrical demand is needed for the endothermic process. The AC electrical power is converted to direct current (DC) power in large rectifying transformers. Brine is electrolyzed to chlorine at the anode and to hydrogen and caustic soda at the cathode.

Electrical power is often made onsite with gas-turbine generators or combined-cycle power facilities. High-pressure steam from the waste-heat boilers is passed through steam-turbines to drive large equipment or additional generators. The reduced pressure steam is used extensively to concentrate 12%-33% caustic soda.

There are three major types of electrolytic processes:

A. Membrane Cell Technology. This is the most modern type and represents about 70% of the installed chlor-alkali capacity.

B. Diaphragm Cell Technology. This has been in existence for many years and represents more than 25% of installed chlor-alkali capacity. Older chlor-alkali facilities started out with asbestos cell technology. Many plants are replacing the asbestos cells with upgraded diaphragm cell technology that does not use asbestos.

C. Mercury Cell Technology. This is being phased out in most of the world’s chlor-alkali production plants. Only a few plants using this technology remain in operation.

Chlorine is an oxidizer material that is highly corrosive and toxic. It is reactive with hydrogen and iron. Chlorine gas will ignite with steel above 300°F (149°C).

Hydrogen is highly flammable and reactive in both air and chlorine. Its explosive range is very wide (4%-75% in air) and its minimum ignition energy (MIE) is very low.

Hydrogen is lighter than air. Ignition is likely in the event of loss of containment if the gas reaches its LEL (lower explosive limit). Sunlight, light static discharge, cell polarity, and fluid velocity discharge can all ignite hydrogen.

Sodium hydroxide (NaOH) is noncombustible as a solid and as an aqueous solution. It is highly corrosive with most metals.

3.2.1 Brine Treatment

Sources of nitrogen, such as amines, ammonia, nitrous oxides and other NH-groups, need to be removed from the raw brine prior to being fed to the cells. These nitrogen-based molecules can lead to the formation of nitrogen trichloride (NCl_3), which is an unstable material. An explosion hazard may be present in process equipment where chlorine is processed or stored (see 3.2.3).

Membrane cells also require high-purity brine. Minerals such as calcium, magnesium and other ions need to be removed from the brine to prevent them from forming precipitates in the solution, which could block the membrane transfer, resulting in tearing and hydrogen migration to the anolyte side.

3.2.2 Prevention of Hydrogen Explosion

Hydrogen explosion hazards are inherent to chlorine production because hydrogen is co-produced during brine electrolysis and can form flammable atmospheres with air, typically via equipment malfunctions and/or procedural errors.

Hydrogen in the chlorine stream can result in an ignition and exothermic reaction of hydrogen with chlorine that can accelerate very rapidly in the entire chlorine system resulting in overpressure. Dilution safeguard systems (DSS) are used to prevent formation of explosive hydrogen atmospheres. The most common dilution media in a DSS is air.

3.2.2.1 Sampling Points and Monitored Reactants

Figure 3.2.2.1 shows a typical diagram for sampling locations and monitored reactants for a generic electrolysis process. Monitoring points are shown at the red and green boxes for oxygen and hydrogen gas, respectively. It may be inferential, continuous, or a combination. Hydrogen is monitored in the chlorine gas headers and tail gas (waste) streams, while oxygen is monitored in the hydrogen stream. Tail gas is the non-condensable gas from the chlorine liquefaction condensers which are sent to be scrubbed, incinerated or consumed in an acid burner.

Dilution safeguard systems (DSS) are commonly located at the electrolyzers for startup purposes due to high hydrogen (H_2) concentrations at the beginning of the process, and the compression and liquefaction phase to keep hydrogen (H_2) concentration to acceptable levels.

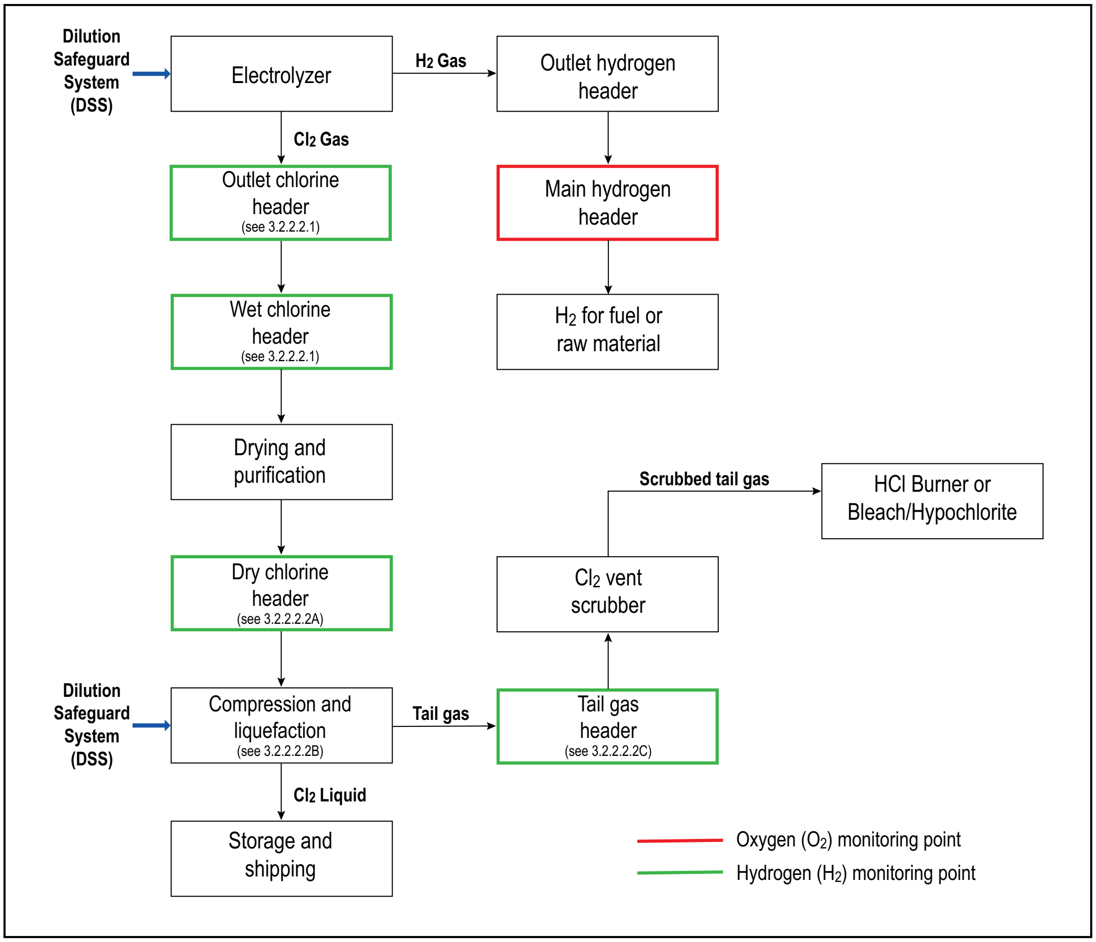

Fig. 3.2.2.1. Typical sampling locations and monitored reactants for dilution safeguard systems used to prevent hydrogen explosions

3.2.2.2 Hydrogen Monitoring Methods

3.2.2.2.1 Wet Gas Monitoring

Continuous or online monitoring is in use at some plants to measure hydrogen concentration in the chlorine headers and tail gas. Technology has advanced to allow for continuous analyzers in both the wet-gas and dry-gas headers. They typically are a conductivity analyzer, gas chromatograph, or mass spectrometer. More recently, solid state sensors have been introduced and are reportedly in field trials. Many chlorine plants may still rely on inferential methods (manual sampling of wet-gas stream such as a buret, which is a titration of HCl to determine H_2 percentages in Cl_2 stream) to test individual cells, circuit headers or the main header.

3.2.2.2.2 Dry Gas Monitoring

Concentrations and alarms for hydrogen (H_2) in dry chlorine (Cl_2) stream have different setting points, stablished according to the process phase, as shown below:

A. After drying tower. Alarms generally set at 1% and can be arranged for alarm or cell shutdown at ~3%

B. After primary liquefaction. Alarms generally set at 4% with auto dilution to reduce H_2 concentration.

C. At tail gas system. Alarms generally set at 5% with auto dilution upstream at primary liquefaction.

3.2.2.3 Hydrogen Concentration Trip and Alarm Settings

Appropriate concentration alarm and trip settings must be established by each site based on the type of monitoring system, PHA findings, and engineering analysis. Process knowledge is also required to balance the need for timely intervention to prevent explosions against increased risk of false trips.

The normal hydrogen concentration varies widely based on the type, age, and stage of the process. Typically, membrane cell technology will be less than 1% and diaphragm cell technology will vary between 1%-2%.

Dilution mediums for DSS, can be compressed air or nitrogen. It is generally recommended that the source be uninterruptible.

3.2.2.4 Startup and Restart After Outage

Most explosions occur during the startup stage. Therefore, it is important to consider the hazards in this non-normal operation mode and include it in the PHA. Diaphragm and membrane cells are started at 50%-60% full load rates. Power is then raised incrementally. Significant gassing occurs. In asbestos diaphragm cells low amperage results in elevated hydrogen levels in the chlorine stream. High hydrogen concentration is present during start-up until a steady state is achieved.

Chlorine stream from cell to liquefaction usually ranges from 75%-100% chlorine, primary liquefaction usually ranges from 45%-65% chlorine and tail gas 10%-20% chlorine.

3.2.3 Cell Monitoring Systems

Cell monitoring systems are an important safeguard in chlor alkali manufacturing. They provide early detection of abnormal operating conditions that can lead to hydrogen migration, membrane failures, cell leaks, abnormal anolyte levels in diaphragm cells, or electrical imbalances. By continuously measuring the voltage of individual cell elements and displaying this information in the control room, operators can assess membrane health and overall cell performance. Early detection enables predictive maintenance, reduces unplanned downtime, and extends membrane and cell life.

High-reliability cell monitoring technologies can also initiate alarms or automatically trip the electrolyzer based on abnormal cell-voltage behavior, preventing premature membrane damage. Key indicators include:

- High absolute cell voltage, indicating abnormal resistance or membrane degradation.
- Difference between average voltage of the complete electrolyzer and individual cell voltage, which can detect localized issues such as blocked brine feed to a single element.
- Low cell voltage, identifying severe membrane damage or short circuit conditions.

Some high-reliability cell monitoring technologies can be designed to meet functional safety requirements, typically achieving SIL 1 or SIL 2 reliability depending on the outcome of the risk assessment. These high integrity systems may support:

- Continuous, real time surveillance of cell integrity
- Automated and reliable shutdown actions
- Predictive analytics and condition based maintenance
- Detailed diagnostics to support early fault detection and troubleshooting

3.2.4 Prevention of Nitrogen Trichloride (NCl_3) Explosions

Nitrogen trichloride (NCl_3) is an unstable compound formed by side-reactions during electrolytic chlorine processing operations. NCl_3 is readily soluble and a relative high boiler that tends to accumulate in liquid chlorine heels. A nitrogen trichloride explosion hazard may be present in process equipment where chlorine is vaporized or liquefied. Storage containers are also potentially subject to nitrogen trichloride accumulation and explosion when emptied by vaporization of the liquid chlorine.

3.2.4.1 NCl_3 Removal and Destruction

The preferred design approach is to use inherently safer processes and technology that limit NCl_3 to very low normal concentrations (few parts per million) with no potential accumulation points. However, certain equipment, such as pre-coolers bottoms, vaporizers/reboilers and storage tanks bottoms, may accumulate liquid chlorine and unavoidably require an NCl_3 removal and destruction process step.

Ultraviolet (UV) light and temperature are the two ways to decompose nitrogen trichloride in equipment and vessels. Chlorine gases exiting membrane cells are relatively high temperature, which will decompose nitrogen trichloride. Chlorine gases exiting diaphragm cells pass through UV light which decomposes nitrogen trichloride.

3.2.4.2 Limiting NCl_3 Concentration (LEL)

Explosive decomposition of NCl_3 in liquid chlorine does not have a well-defined lower explosive limit. Euro Chlor, based on reported experimental results, states that “concentration of NCl_3 in solutions greater than 3% w/w at ambient temperature is capable of an accelerated decomposition, which is strongly exothermic. This concentration should also never be reached at any time.”

The Chlorine Institute states that “decomposition of 6-8% nitrogen trichloride in chlorine can result in a significant pressure rise in the vessel containing the chlorine depending on the amount of vapor space in the vessel.”

3.2.4.3 NCl_3 Trips and Monitoring

According to Euro Chlor, in order to avoid reaching a concentration level of 3%, the NCl_3 needs to be limited to 1% by weight in any part of the installation where NCl_3 can build up during normal operation and shutdown. In addition, it is recommended that where frequent checks are not carried out, this limit needs to be reduced to 0.1% or 1000 ppm (w/w). Euro Chlor also recommends a limit of 1000 ppm in all reboilers, vaporizers, and residues obtained when emptying stock tanks.

By comparison, the upper limit on NCl_3 concentration in chlorine recommended by the Chlorine Institute (to avoid reaching 6% nitrogen trichloride) is 2% by weight. This limit applies to any part of the process where NCl_3 can concentrate during normal operations, shutdowns, special procedures, and transient conditions.

For FM, the key considerations when establishing trips and monitoring frequencies need to be based on all of the following:

- Process hazards analyses and engineering studies
- Known baseline (normal range) NCl_3 concentrations
- Ongoing supervision and periodic review/updating of sampling frequencies and procedures
- Euro Chlor and/or Chlorine Institute guidelines
- Active, documented management of change procedures to avoid the introduction of new nitrogen trichloride sources or accumulation points

3.2.4.4 NCl_3 Monitoring Methods and Frequency

Most plants monitor NCl_3 concentration by inferential (intermittent) sampling because instrumentation for continuous measurement remains under development. The frequency of measurement is based on normal concentrations and operating experience. Euro Chlor recommends frequencies be established based on experience and the extent of variation in the results.

4.0 REFERENCES

4.1 FM

Data Sheet 1-57, *Plastics in Construction*
Data Sheet 3-26, *Fire Protection for Non-Storage Occupancies*
Data Sheet 5-31, *Cables and Bus Bars*
Data Sheet 5-4, *Transformers*
Data Sheet 6-13, *Waste Fuel-Fired Facilities*
Data Sheet 7-43, *Process Safety*
Data Sheet 7-78, *Industrial Exhaust Systems*
Data Sheets 7-95, *Compressors*
Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*
Data Sheet 10-8, *Operators*

APPENDIX A GLOSSARY OF TERMS

Dilution safeguard systems (DSS): Prevents process equipment explosions by maintaining a potentially reactive mixture in a dilute state (i.e., below the lower explosive limit). The mixtures will most often be in a gaseous state, but the DSS concept can also be applied to unstable materials dissolved ina liquid phase, such as NCl_3 dissolved in liquid chlorine. Dilution safeguard systems utilize various instruments, devices, and operator procedures to monitor a selected reactant concentration and intervene, when required, to prevent formation of an explosive atmosphere.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

April 2026. Interim revision. The following changes were made:

A. Deleted Section 3.2.2.4 for partial solutions for inferential monitoring systems and created Section 3.2.3 for cell monitoring systems.

July 2024. Interim revision. Minor editorial changes were made.

January 2023. Interim revision. Minor editorial changes were made.

October 2020. This is the first publication of this document.