WCC Cardinal rules

Thomas Vanfleteren,

Technical & Safety Manager – Euro Chlor

WCC Safety Seminar - 14 October 2025

Vancouver, Canada

The 10 WCC Cardinal Rules

1. Remain in safe concentration range for hydrogen in chlorine
2. Use titanium only with wet enough chlorine
3. Ensure low moisture content for dry chlorine handling and uses
4. Control chlorine maximum temperature to avoid iron fire
5. Avoid contact between chlorine and organics
6. Avoid formation/concentration of nitrogen trichloride
7. Write operating procedures/manage the changes
8. Ensure sufficient training/information of all staff
9. Prepare and test emergency response plans
10. Do not forget incident investigation and experience sharing

1. Remain in safe concentration range for hydrogen in chlorine

Explosion risk if hydrogen concentration in chlorine is between around 3 and 93 %

(precise values vary according to pressure, temperature, presence of other components …)

Temperature °C	Minus 60	Minus 40	Minus 20	0	25	50	100
H_2 - Cl_2 vol% H_2	5.0 – 90.0	4 – 90.5	4 – 91.5	3.5 - 92	3 – 92.5	3 - 93	3 - 93

References:

- Euro Chlor: GEST 91/168 - *Physical, Thermodynamic & selected Chemical properties of Chlorine; Chapter 9 – Safety*; 4th Ed. January 2017
- Chlorine Institute Pamphlet 121, *Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine*. Ed 4. March 2016.

1. Remain in safe concentration range for hydrogen in chlorine

Factors increasing H_2 content in Cl_2

- Bad brine quality
- Damaged membrane/diaphragm
  - Failing delta pressure control
  - Failing temperature control
- Hydrogen can also be produced downstream from steel corrosion
- Increases also when chlorine is liquefied

1. Remain in safe concentration range for hydrogen in chlorine

In addition to preventative actions, additional monitoring is strongly recommended:

- For all processes; in line measurement of H_2 in Cl_2
  - At electrolyser level
  - In liquefaction process
- For membrane process; cell voltage monitoring system
  - Pinhole detection options
  - High voltage (e.g. in case of brine or catholyte blockage)
  - Difference between single cell voltage and average
  - Low voltage (in case of severe leaks or shortcuts)

1. Remain in safe concentration range for hydrogen in chlorine

- **Example of hydrogen/chlorine explosion in gaseous chlorine pipeline to customer**

2. Use titanium only with wet enough chlorine

Never Expose Titanium to Dry Chlorine*

If chlorine is not wet enough, titanium will burn!

$$2\,Cl_2 + Ti \xrightarrow[< 0.4wt\%\ H_2O]{} TiCl_4 + HEAT$$

If water is present, titanium preferably reacts with water to form a protective titanium oxide layer, preventing the titanium from reacting with chlorine

Some aspects to consider:

- Low temperatures reduce moisture content
- High pressures reduce moisture content
- High surface areas *increase* the required moisture content

⇒ Monitor temperature

⇒ Add water vapour if necessary

⇒ Do not mix stainless steel and titanium!

*Chlorine with < 0.4wt% H_2O at room temperature

WORLD chlorine council®

2. Use titanium only with wet enough chlorine

Titanium thermometer well in dry chlorine!

3. Ensure low moisture content for dry chlorine handling and uses

Never expose carbon steel to wet chlorine

- **With dry chlorine, a protective layer of $FeCl_3$ is formed**
  - $FeCl_3$ can form all kinds of hydrates ($FeCl_3.xH_2O$)
  - Hydrates can melt and cause severe corrosion (>180 mm/year)

3. Ensure low moisture content for dry chlorine handling and uses

Heat exchanger corroded by wet chlorine: chlorine leak into water and emission via cooling tower…

⇒ Dry equipment thoroughly before putting it into service

⇒ Control drying towers (concentration and temperature of sulphuric acid)

⇒ Use moisture on-line analysers

References:

- Euro Chlor: GEST 10/362 - Corrosion Behaviour of Carbon Steel in Wet and Dry Chlorine; Edition 4 November 2022

4. Control chlorine maximum temperature to avoid iron fire

Never expose iron to too high temperatures

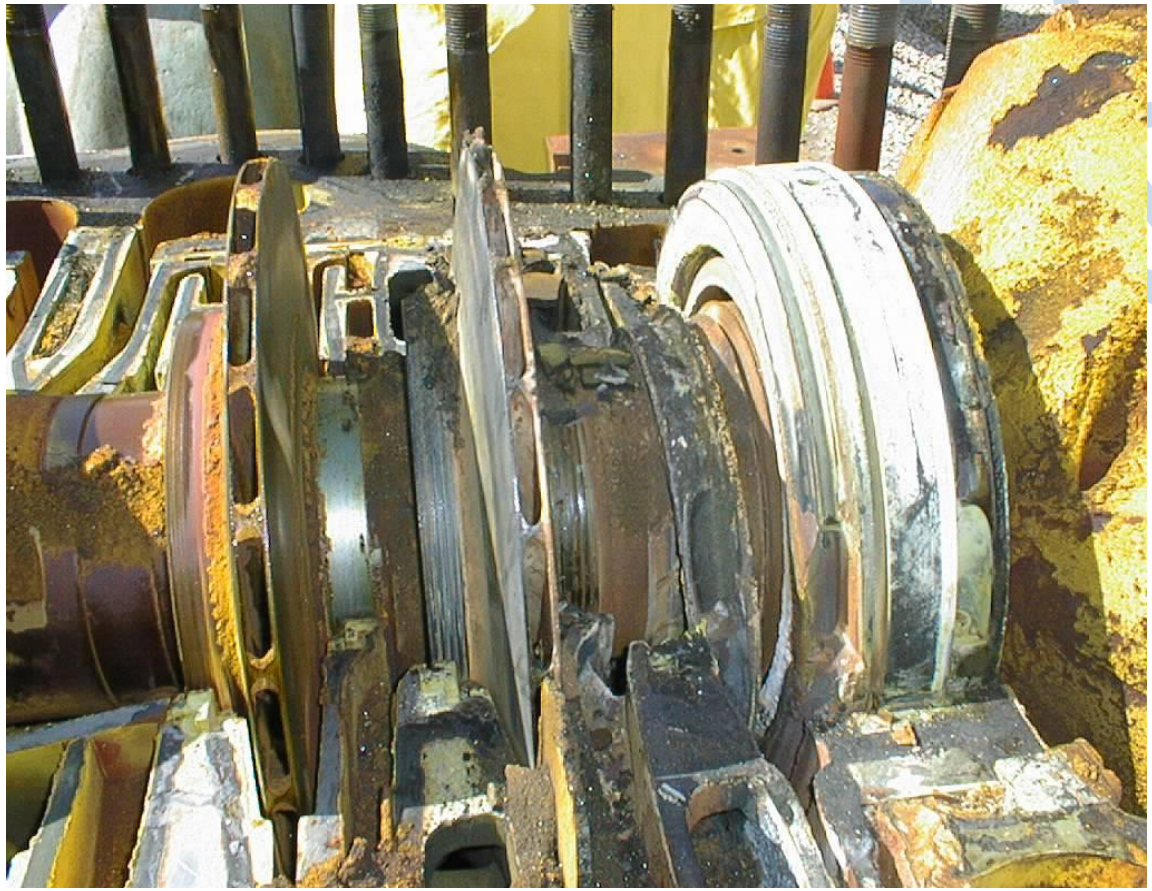
- **Protective layer is $FeCl_3$**
- **But $FeCl_3$ has a vapour pressure**
  - Boiling point of $FeCl_3$ is 315 °C
  - As of 120 °C, vapour pressure becomes significant
  - And reaction $2\ Fe + 3\ Cl_2 \longrightarrow 2\ FeCl_3$ + heat
  - At certain temperatures, it happens so quickly that fire occurs
- **Many factors will impact the exact temperature of ignition**
- **To prevent fire, Euro Chlor recommends a system temperature below 120 °C**

References:
- Euro Chlor: GEST 10/362 - Corrosion Behaviour of Carbon Steel in Wet and Dry Chlorine; Edition 4 November 2022

4. Control chlorine maximum temperature to avoid iron fire

Initiating Events

- Mechanical rub
- Foreign object
- Failure of cooling systems
- High pressures
- Failure of heat tracing
- Excessive process heat



4. Control chlorine maximum temperature to avoid iron fire

Preventive measures:

- ⇒ Ensure reliable cooling
- ⇒ Keep heat tracing under strict control
- ⇒ Use high temperature trips

5. Avoid contact between chlorine and organics

Non-fully halogenated organic compounds can react exothermically with chlorine, causing iron fire …

⇒ Degrease equipment completely where possible

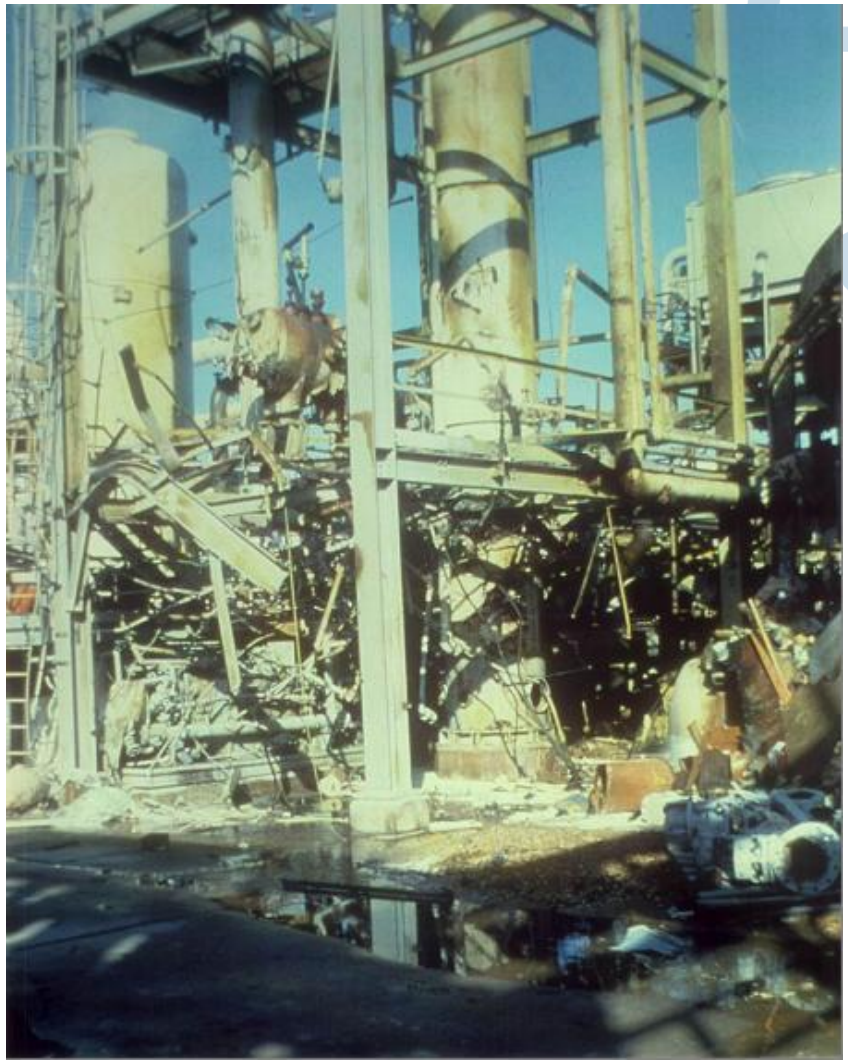
⇒ Use only greases and oil fully compatible with chlorine where contact is possible

⇒ Avoid any possible backflow from downstream user's plant

Refer to CI Pamphlet 6) *Piping Systems for Dry Chlorine* and
CI Pamphlet 164) *Reactivity and Compatibility of Chlorine and Sodium Hydroxide with Various Materials*

5. Avoid contact between chlorine and organics

Consequences of chlorine – organic reaction can be disastrous!



6. Avoid formation/concentration of nitrogen trichloride

- Reaction of nitrogen compounds in electrolysis cells to form NCl_3 (very strong explosive)
- Unstable oily product, less volatile than chlorine: accumulates where liquid chlorine is vapourised

⇒ Check all possible sources (salt, added water / HCl / caustic soda, ammonia from cooling systems …)

⇒ Eliminate nitrogen compounds from brine

⇒ Periodically analyse brine and chlorine or continuously measure NCl_3 in gas phase

⇒ Destroy NCl_3 before reaching too high concentration

6. Avoid formation/concentration of nitrogen trichloride

Explosion in chlorine purification column

Explosion in pipeline

References:

- Euro Chlor: GEST 76/55 - Maximum Levels of Nitrogen Trichloride in Liquid Chlorine ; Edition 14; November 2021
- CI Pamphlets: 21) Nitrogen Trichloride - A Collection of Reports and Papers and 152) Safe Handling of Chlorine Containing Nitrogen Trichloride

7. Write operating procedures/manage changes

- Procedures (and technical documentation) must be
  - Written with participation of field staff
  - Periodically checked and updated
  - Known by staff
  - Kept alive with regular training

- Even minor modifications, including for improvement, must be examined by HAZOP or similar risk study.

8. Ensure sufficient training/information of all personnel

- Concerns own staff, as well as contractors
- Integration of field expertise in
  - Hazard analysis / procedures
  - Plant audits
  - Incident investigations
- Do not forget refresher training …
- We noticed an increase in incidents due to lack of training or inadequate procedures over the past couple of years (after Covid)

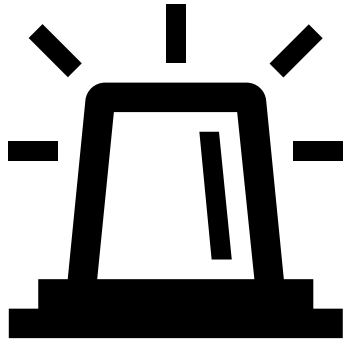
8. Ensure sufficient training/information of all staff

Non-hazardous smoke machine training exercise

- Using stage smoke to simulate limited visibility and level A suits to demonstrate limited dexterity, trainees participated in exercise to stop leak
- Mimic real events, operators needs to know how to react under pressure

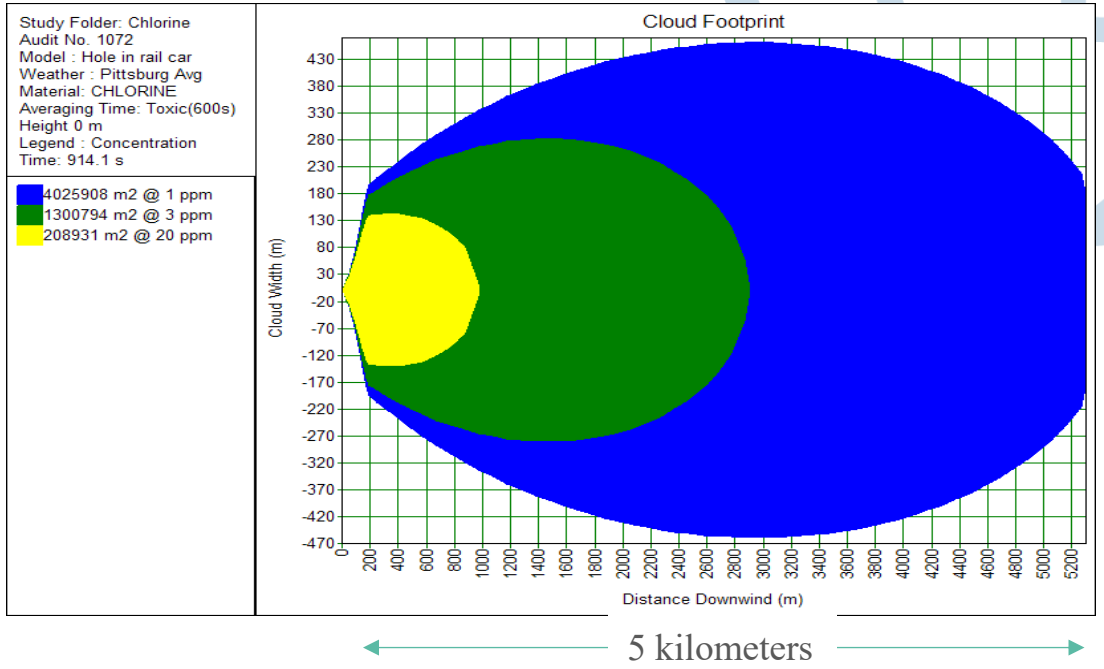
9. Prepare and test emergency response plans

- Establish relationships with local authorities before emergencies arise
- Inform relevant stakeholders
- Simulate and exercise periodically



9. Prepare and test emergency response plans

Example of chlorine release and modelling software



Dispersion models are used to predict the area impacted by chlorine release; improved models from Jack Rabbit experiments are regularly published
See the Chlorine Institute explanatory video here

10. Do not forget incident investigation and experience sharing

- Important to analyse causes and find out what to do to avoid similar incidents
- Incident reports:
  - Description
  - Investigation of results
  - Root causes
  - Corrective action and lessons learned
- Information used by associations to improve technical recommendations/ pamphlets, and also for drawing up WCC guidelines
- Also included in quarterly publication of WCC GST Newsletter

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THANK YOU !

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