

# Hydrogen safety in chlor-alkali

*Ton Manders Euro Chlor*



**CloroSur**  
**2022**

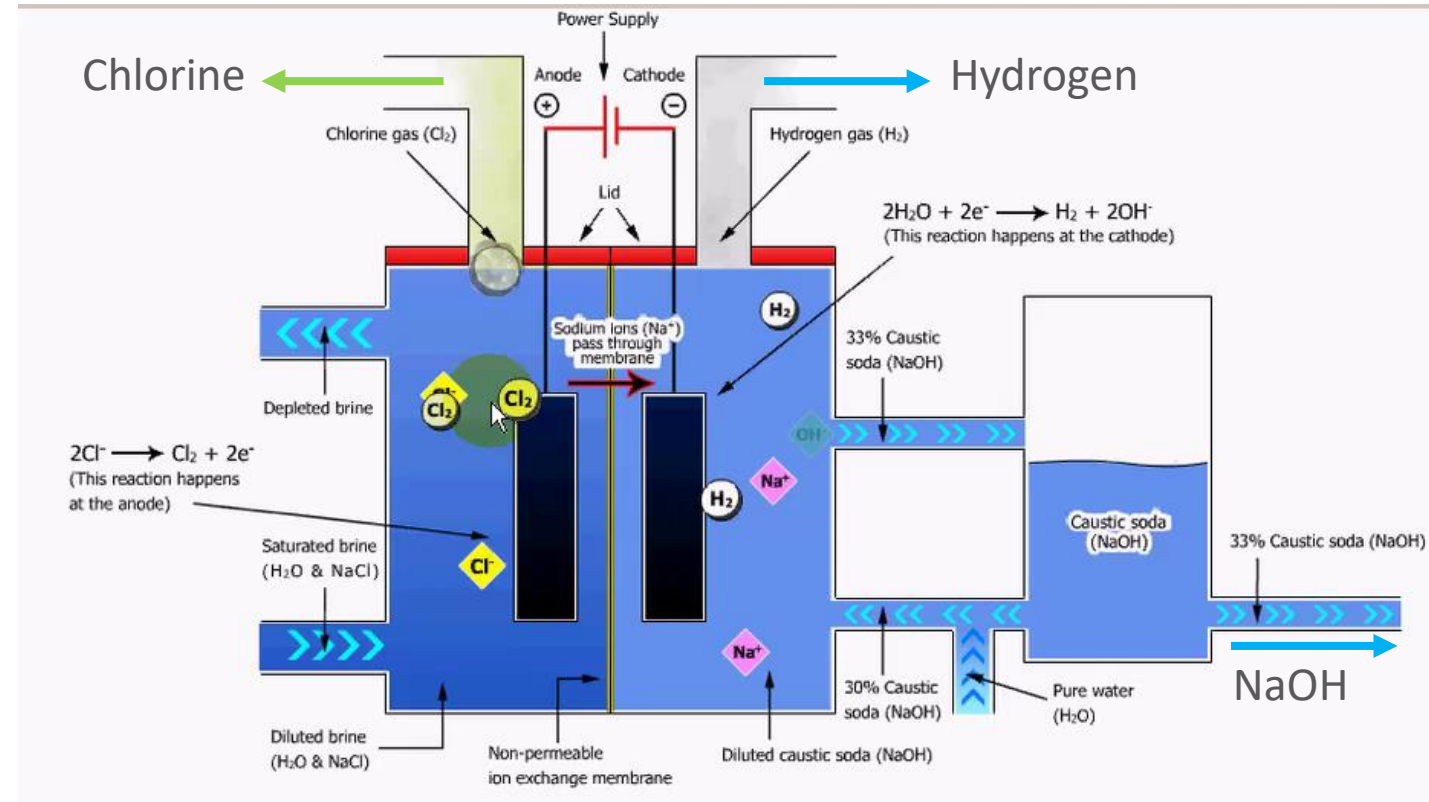
COSTA DO SAUÍPE

# Content

- **Introduction**
- **Explosion limits**
  - **The risks in a chlorine plant**
  - **Electrolysers**
  - **Chlorine cooling & liquefaction**
  - **Chlorine absorption**
  - **Catholyte circulation, caustic evaporation, caustic storage**
  - **Hydrogen cooling**
  - **HCl production & Acid tanks**
- **Conclusions**

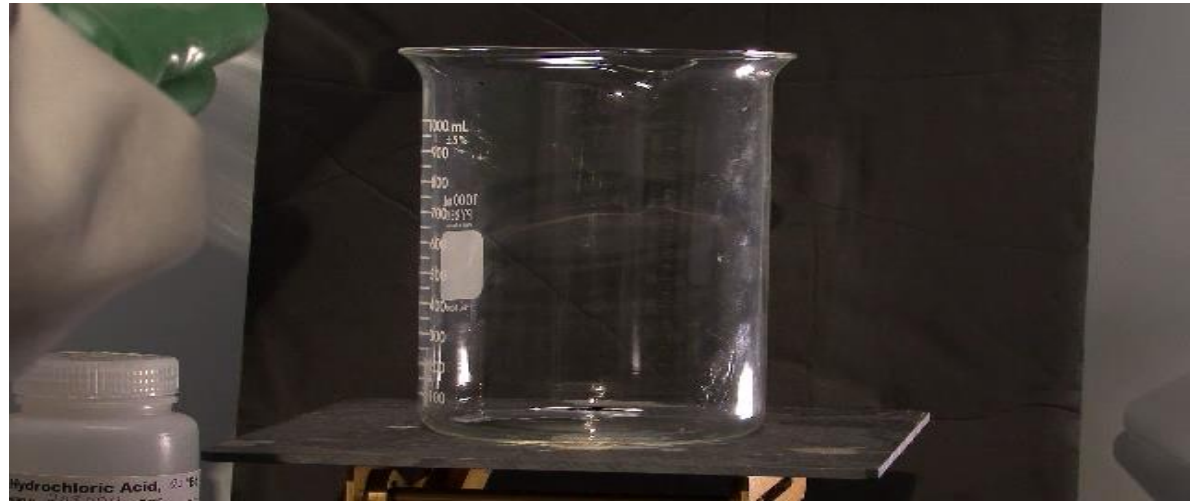
# Introduction

- Production of chlorine and hydrogen are coupled
  - $2\text{NaCl} + 2\text{H}_2\text{O} \longrightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH}$
- Unless you use the ODC process
  - $2\text{NaCl} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \longrightarrow \text{Cl}_2 + 2\text{NaOH}$
- $\text{H}_2$  can be more or less in every part of the chlor-alkali installation
- The electrolyser is not the only source of the  $\text{H}_2$



# Introduction

- Other H<sub>2</sub> sources in the chlor-alkali installation
  - Acid (e.g. HCl, H<sub>2</sub>SO<sub>4</sub>) in contact with metals generates H<sub>2</sub>



Video: Aluminum foil + HCl solution

- Melting FeCl<sub>3</sub>.x<sub>aq</sub> can create an acid environment and the acid can react with the metal and form H<sub>2</sub>



# Explosion limits

- Explosion limits and the effect of temperature<sup>1)</sup>
  - The effect of pressure is limited<sup>1)</sup> for chlorine the lower explosion limit become 2.5 – 3 vol% at 13.5 bar(a)

Temperature in °C	H <sub>2</sub> – Air (vol% H <sub>2</sub> )	H <sub>2</sub> – O <sub>2</sub> (vol% H <sub>2</sub> )	H <sub>2</sub> – Cl <sub>2</sub> (vol% H <sub>2</sub> )
Minus 60	4.0 - 69	4.0 - 96	5.0 - 90.0
Minus 40	4.0 - 71	4.0 - 96	4.0 - 90.5
Minus 20	4.0 - 72	4.0 - 96	4.0 - 91.5
0	4.0 - 73	4.0 - 96	3.5 - 92.0
20 – 25	4.0 - 75	4.0 - 96	3.0 - 92.5
50	3.7 - 76	4.0 - 96	3.0 - 93.0
100	3.0 - 80	4.0 - 97	3.0 - 93.0

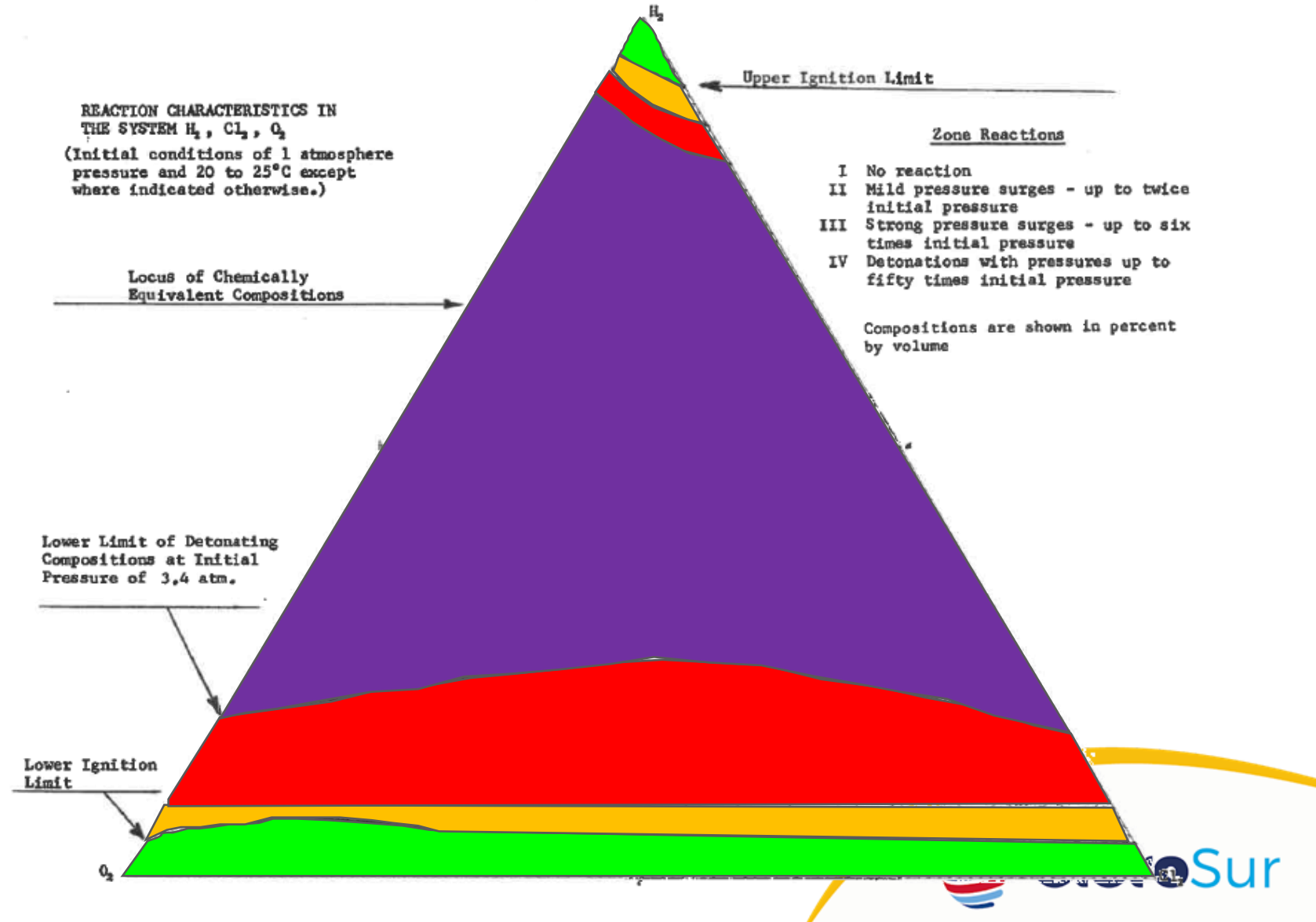
- Ignition energy is very low 10<sup>-7</sup> J
- Auto ignition temperature H<sub>2</sub> – Cl<sub>2</sub> mixtures is 207 °C (for H<sub>2</sub>-air it is 400 °C)

<sup>1)</sup> See GEST 91/168 Chapter 9

# Explosion limits in the system $\text{Cl}_2 - \text{H}_2 - \text{O}_2$

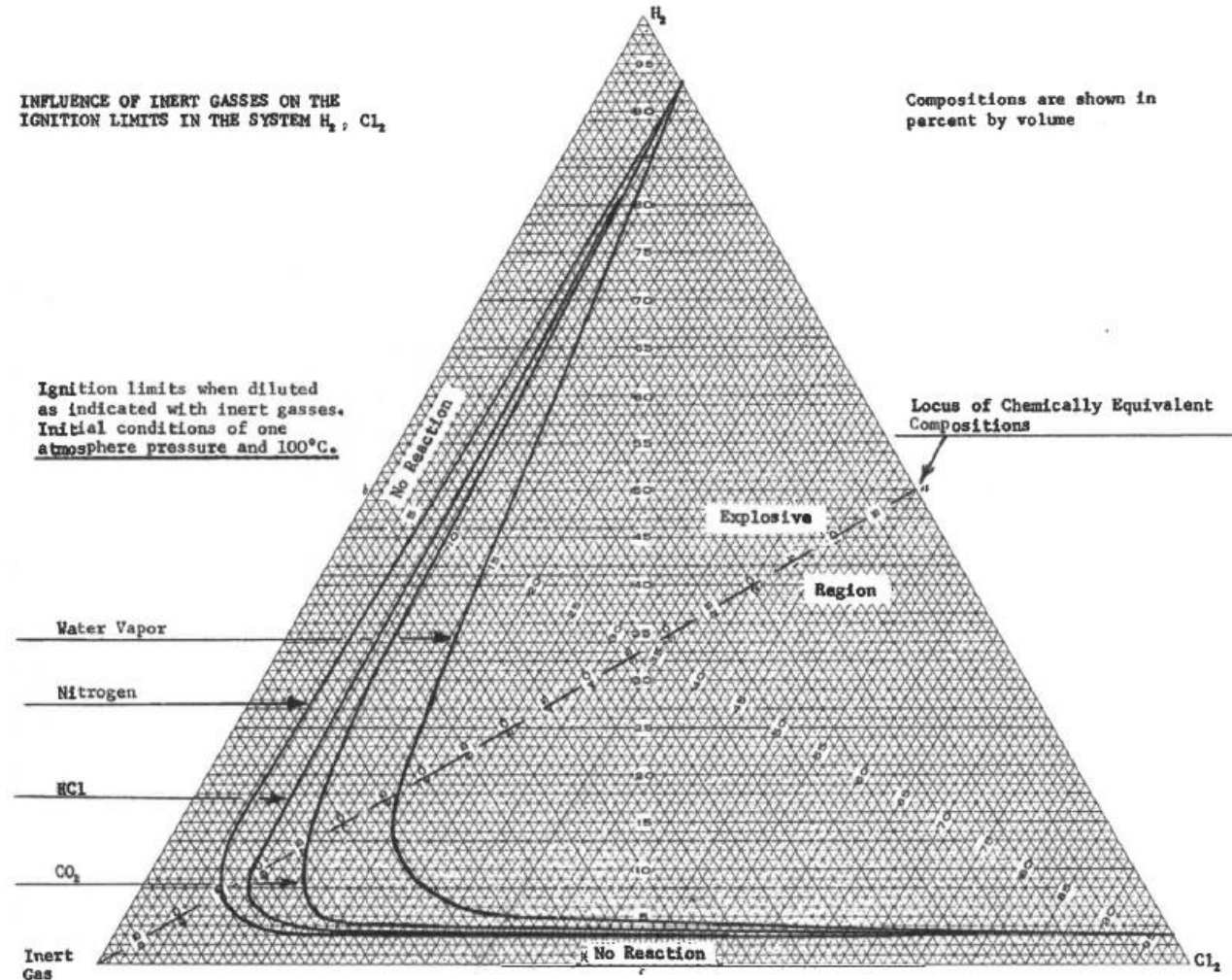
- Explosion limits

- No reaction
- Mild explosion 2 times initial pressure
- Strong explosion 6 times initial pressure
- Detonations 50 times initial pressure



# Explosion limits

- Effects of Inert gases is limited



# The risks in a chlorine plant

## Electrolysers

- Normal operating conditions:
  - Cl<sub>2</sub>: 97.0 – 99.9 vol% (dry basis)
  - O<sub>2</sub>: 0.1 – 2.5 vol% (dry basis)
  - H<sub>2</sub>: 0.0 – 0.5 vol% (dry basis)
  - H<sub>2</sub>O: 40.0 – 60.0 vol% (highly influenced by operating temp.)
- Water reduces the concentrations and consequently, the risk of having an explosive mixture
- **Caution**: water concentration decreases dramatically during cooling and drying of the Cl<sub>2</sub>-gas, **So do not count on the dilution effect of water**
- **Main risk**: when hydrogen levels increase above normal; e.g. membrane leakages



# The risks in a chlorine plant

## Electrolysers

- Preventive measures

- Purge with nitrogen when taking electrolyzers out of operation
- Measure hydrogen in chlorine gas (early detection/early warning)
- Have a cell voltage monitoring system (early detection/warning for leaking membranes)
- Be aware that condensate from hydrogen system is saturated with hydrogen, have sufficient dilution air or purge collection systems continuously with nitrogen
- The cell room has normally not an explosion proof (ATEX) design; but take care that hydrogen cannot accumulate in the top of the roof

# The risks in a chlorine plant

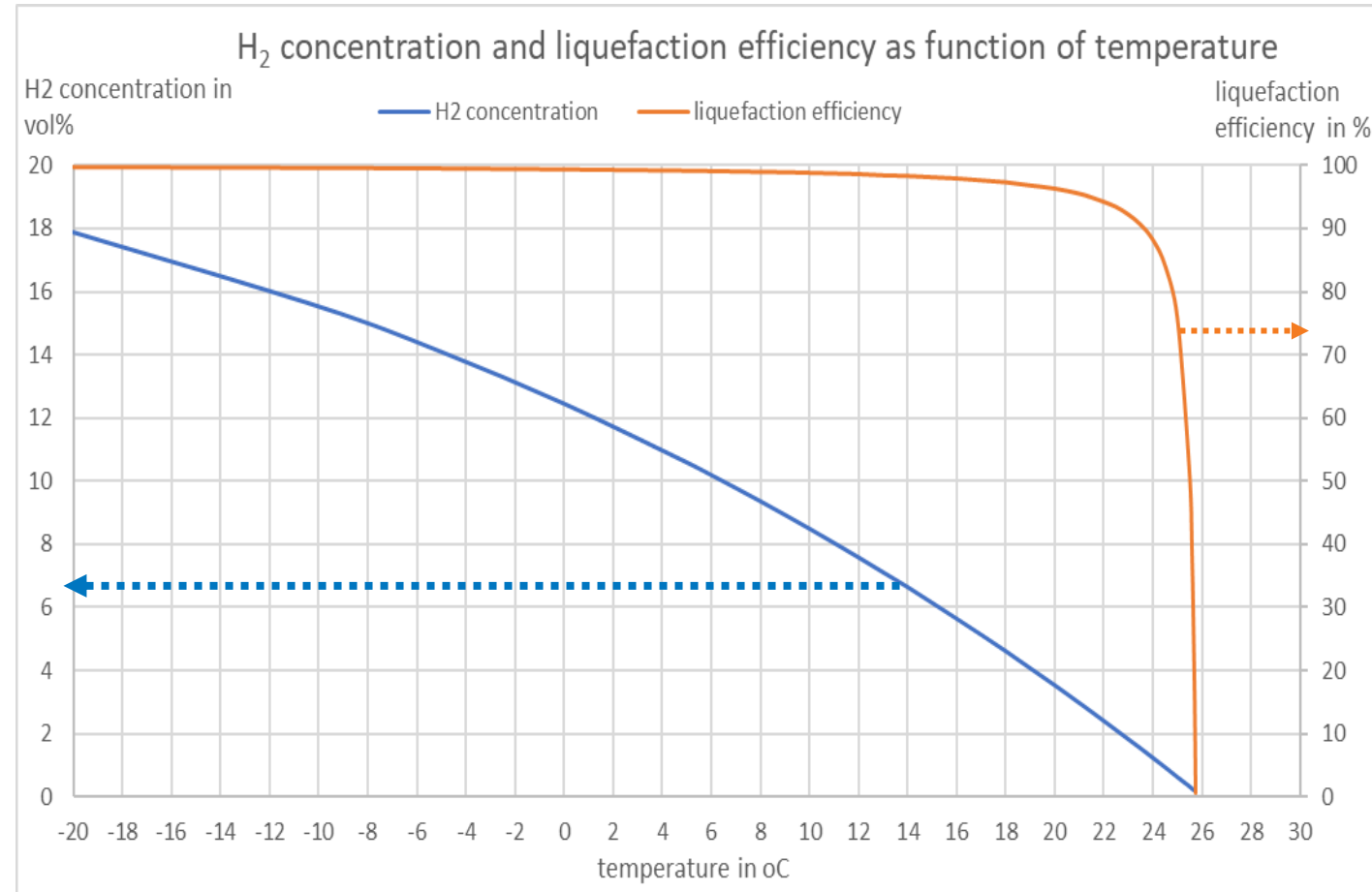
## Chlorine cooling and liquefaction

- During the cooling and drying the water will be removed but the hydrogen concentration (on dry basis) doesn't change. Normal operating conditions:
  - Cl<sub>2</sub>: 97.0 – 99.9 vol% (dry basis)
  - O<sub>2</sub>: 0.1 – 2.5 vol% (dry basis)
  - H<sub>2</sub>: 0.0 – 0.5 vol% (dry basis)
- **Main risk**: when hydrogen levels increase above normal; e.g. membrane leakages the risk of an explosive mixture increase
- During the chlorine liquefaction the H<sub>2</sub> and O<sub>2</sub> concentration starts to increase; With an increasing risk of getting an explosive mixture.
  - Especially when hydrogen concentration increases in gas from electrolyzers e.g. due to membrane damages

# The risks in a chlorine plant

## Chlorine cooling and liquefaction

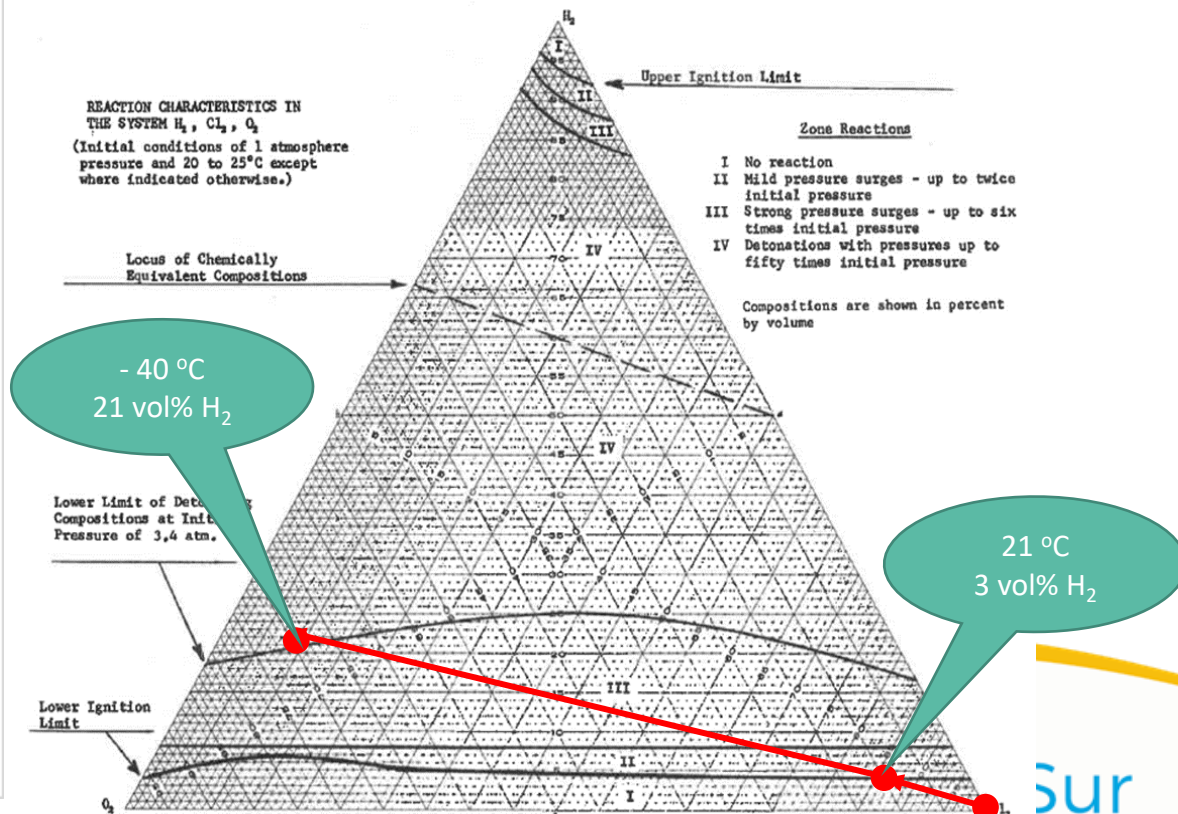
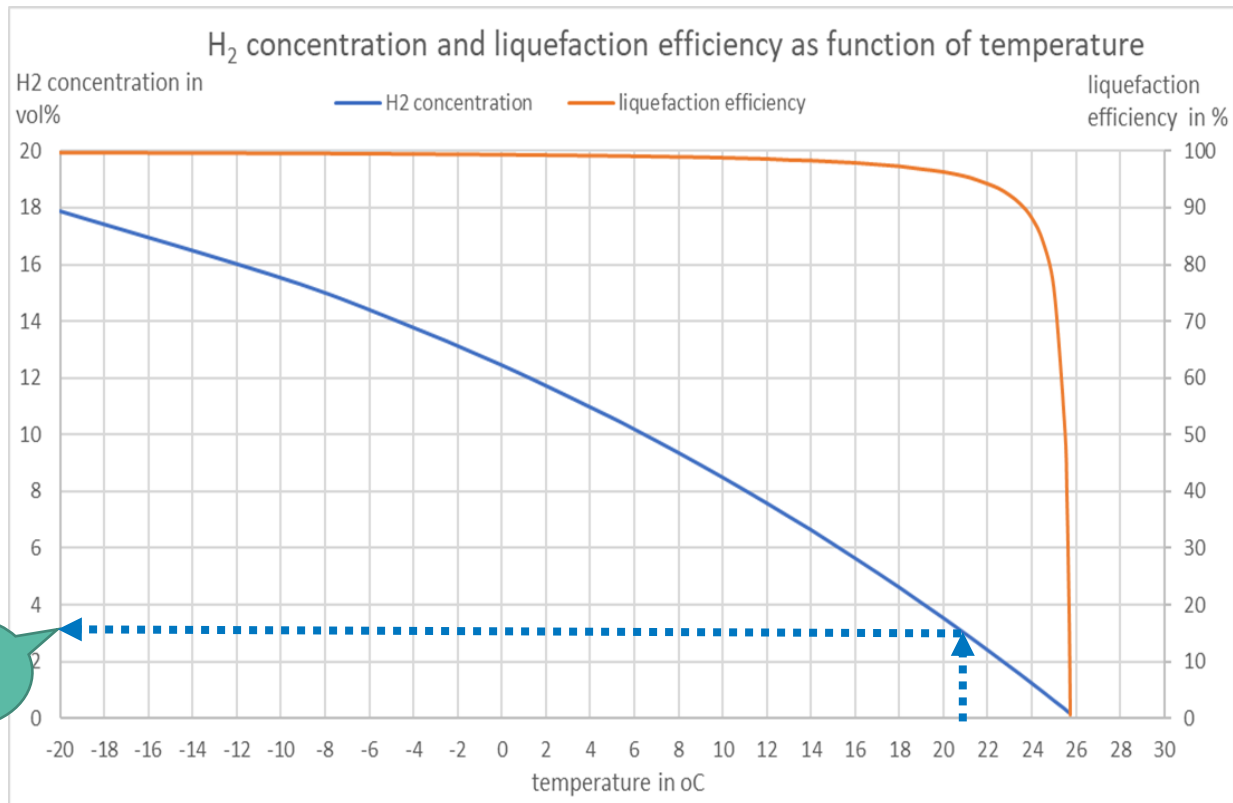
- Assume the following conditions:
  - Cl<sub>2</sub>: 99.35 vol%
  - O<sub>2</sub>: 0.50 vol%
  - H<sub>2</sub>: 0.15 vol%
  - 8 bar(abs) and 90 °C
- Condensation starts at 25.8 °C
  - In the graph, H<sub>2</sub> concentration is presented as a function of the condensation temperature



# The risks in a chlorine plant

## Chlorine cooling and liquefaction

- At temperatures  $< 21\text{ }^{\circ}\text{C}$  the gas mixture is explosive
  - Liquefaction efficiency 96%
- At temperatures  $< -40\text{ }^{\circ}\text{C}$  the gas mixture is in the detonation zone



# The risks in a chlorine plant

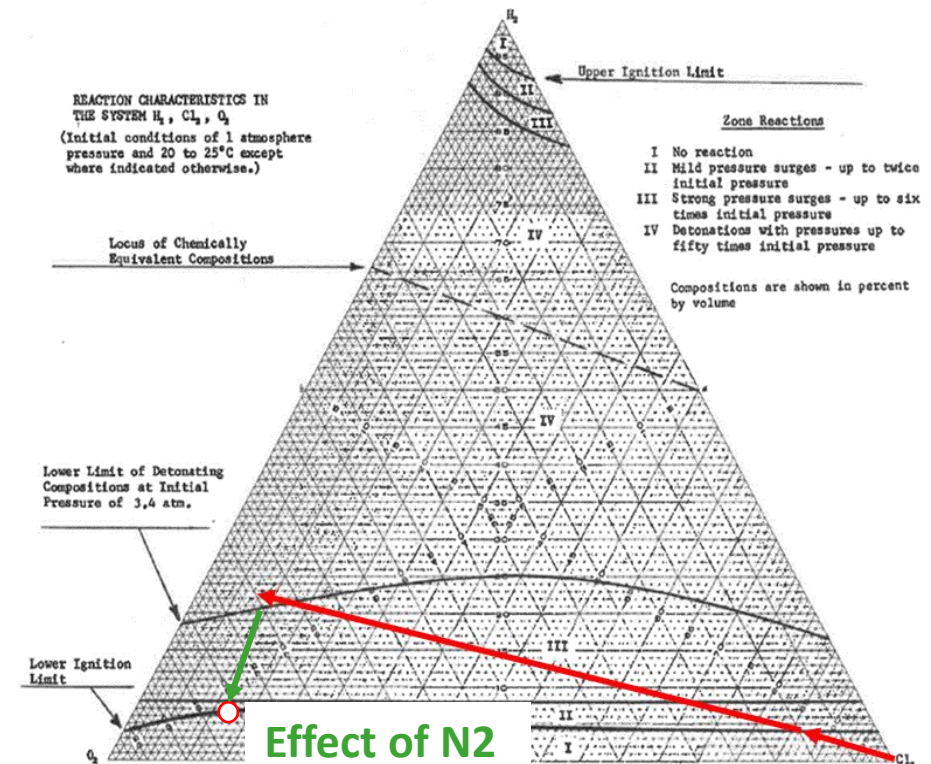
## Chlorine cooling and liquefaction

- Preventive/control measures

- Measure hydrogen in chlorine gas at electrolyzers (early detection/early warning)
- Have a cell voltage monitoring system (early detection/warning for leaking membranes)
- Measure  $H_2$  concentration after each condensation step and use this to control temperature of the condensation and/or nitrogen intake

- Safe guards:

- Have a safety function at high  $H_2$  concentration:
  - Stop production and purge with  $N_2$
- Make condensation system explosion proof



# The risks in a chlorine plant

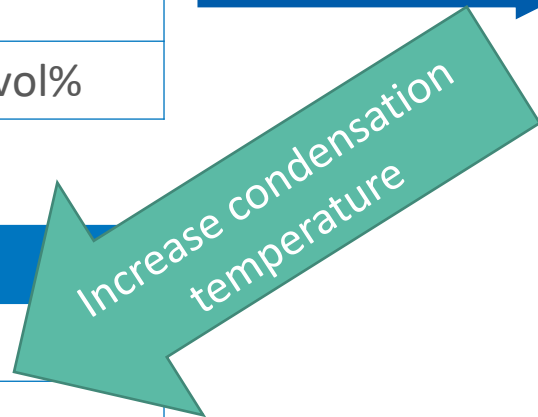
## Chlorine cooling and liquefaction

- What happens if (suddenly) the H<sub>2</sub> level in the gas from the electrolyser increases?
- Take the previous example; assume H<sub>2</sub> in cell gas increases from 0.15% to 0.3%

Cl <sub>2</sub> :	99.35 vol%
O <sub>2</sub> :	0.50 vol%
H <sub>2</sub> :	0.15 vol%
8 bar(abs) & condensation at 21 °C	
H <sub>2</sub> concentration after condenser 2.9 vol%	



Cl <sub>2</sub> :	99.20 vol%
O <sub>2</sub> :	0.50 vol%
H <sub>2</sub> :	0.30 vol%
8 bar(abs) & condensation at 21 °C	
H <sub>2</sub> concentration after condenser <b>4.81 vol%</b>	



Cl <sub>2</sub> :	99.20 vol%
O <sub>2</sub> :	0.50 vol%
H <sub>2</sub> :	0.30 vol%
8 bar(abs) & condensation at <b>23 °C</b>	
H <sub>2</sub> concentration after condenser <b>2.94 vol%</b>	

Add .5vol%  
N<sub>2</sub>/dry-air

Cl <sub>2</sub> :	99.20 vol%
O <sub>2</sub> :	0.50 vol%
H <sub>2</sub> :	0.30 vol%
8 bar(abs) & condensation at 21 °C	
H <sub>2</sub> concentration after condenser <b>2.96 vol%</b>	

# The risks in a chlorine plant

## Chlorine cooling and liquefaction

- Why does the decrease of electrolyser load not help?
- The upset is probably caused by an increase in “pinholes” in membranes
- Increased holes means increased flow of hydrogen to chlorine
- Lower production doesn't decrease the  $H_2$  through the membrane, it only decreases the chlorine production and (slightly) the  $H_2$  production of the leakage current
  - Effect =  $H_2$  concentration in chlorine increases even further
  - **Wrong measure**

# The risks in a chlorine plant

## Chlorine absorption

- In  $\text{Cl}_2$  absorption all kind of gasses containing  $\text{Cl}_2$  are treated
- These gases will also contain  $\text{H}_2$
- In the absorption,  $\text{Cl}_2$  will react but  $\text{H}_2$  and  $\text{O}_2$  remain
- Risk of getting explosive mixtures
- Measure:
  - Always ensure sufficient air or nitrogen flow to absorption to ensure under all conditions sufficient low  $\text{H}_2$  concentrations



# The risks in a chlorine plant

## Catholyte circulation, caustic evaporation, caustic storage

- The caustic from the electrolyzers is saturated with  $H_2$
- The caustic circulation tank normally connected with  $H_2$  system,
  - So only gas bubbles will be released, caustic will remain saturated
- If caustic is further concentrated in an evaporation the hydrogen will escape together with the water vapor
  - Check if the vent system/vacuum system of the caustic evaporation can contain explosive mixtures
- For the storage (mainly for caustic from electrolyzers) ensure that hydrogen cannot accumulate in the top of storage tanks
  - E.g. have a small  $N_2$  purge on the storage tanks

# The risks in a chlorine plant

## Hydrogen cooling

- The hydrogen cell gas will normally be cooled
  - The condensate will be saturated with H<sub>2</sub>
  - Be aware: spaces above open drains and trenches might be flammable
    - Important awareness for work activities around these area's as the environment may eb explosive
- Hydrogen vent stack
  - Ensure that there is no possibility for ingress of air into the hydrogen system
    - e.g. a continuous positive flow of N<sub>2</sub> and/or a water seal

# The risks in a chlorine plant

## HCl production and Acid tanks

- In the HCl production (from  $\text{Cl}_2 + \text{H}_2$ ) normally and excess  $\text{H}_2$  is used.
  - Ensure the vent gas outlet is at a safe place
  - The vent gas stream can be flammable and/or explosive
  - The produced HCl solution is saturated with  $\text{H}_2$
  - Ensure adequate venting and blanketing practices
- Hydrochloric acid storage tanks
  - $\text{H}_2$  can come from the saturated HCl solution from the HCl production
  - $\text{H}_2$  generation due damaged protective layer (of metal tanks)
  - Ensure adequate venting and blanketing practices

# Conclusions

- $\text{Cl}_2$  will always contain a small amount of  $\text{H}_2$
- Dangerous situations can occur everywhere in the process
- It is advised to measure hydrogen:
  - After the electrolyzers
  - After the condensation or in between the different condensation steps
- Have sufficient control in the condensation when  $\text{H}_2$  levels increase
  - Adding  $\text{N}_2$  or (dry) Air
  - Increase condensation temperature
- Always add sufficient amounts of fresh air to the absorption to avoid explosive/detonative mixtures

# Conclusions

- H<sub>2</sub> can not only cause problems in the chlorine system
- Be aware of hydrogen releases and thus potential risks of fire/explosions in
  - Hydrogen condensate system
  - Caustic evaporation
  - Caustic storage
  - Hydrochloric acid production
  - Acid storage tanks
- Install sufficient measure to avoid accumulation of H<sub>2</sub>

A tropical landscape featuring a body of water in the foreground, a line of palm trees on a small island in the middle ground, and a blue sky with scattered white clouds. A large, semi-transparent yellow shape is overlaid on the image, containing the text.

**Thank You**  
**Ton Manders (tma@cefic.be)**