Safety around Hydrogen in chlorine

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Overview

- Chlorine generated in electrolysis inevitably contains hydrogen
- Drying chlorine gas, condensing chlorine gas and absorbing chlorine gas increase the hydrogen concentration of the remaining gas
- Hazard: Explosion of gas wherein the hydrogen concentration exceeds the Lower Explosion Limit (LEL)
- Normal operation of membrane electrolysis and downstream processes
- Startup and shutdown aspects
- Failure scenarios resulting in increase of hydrogen concentration
- Securing safe operation

Lower explosion limit (LEL)

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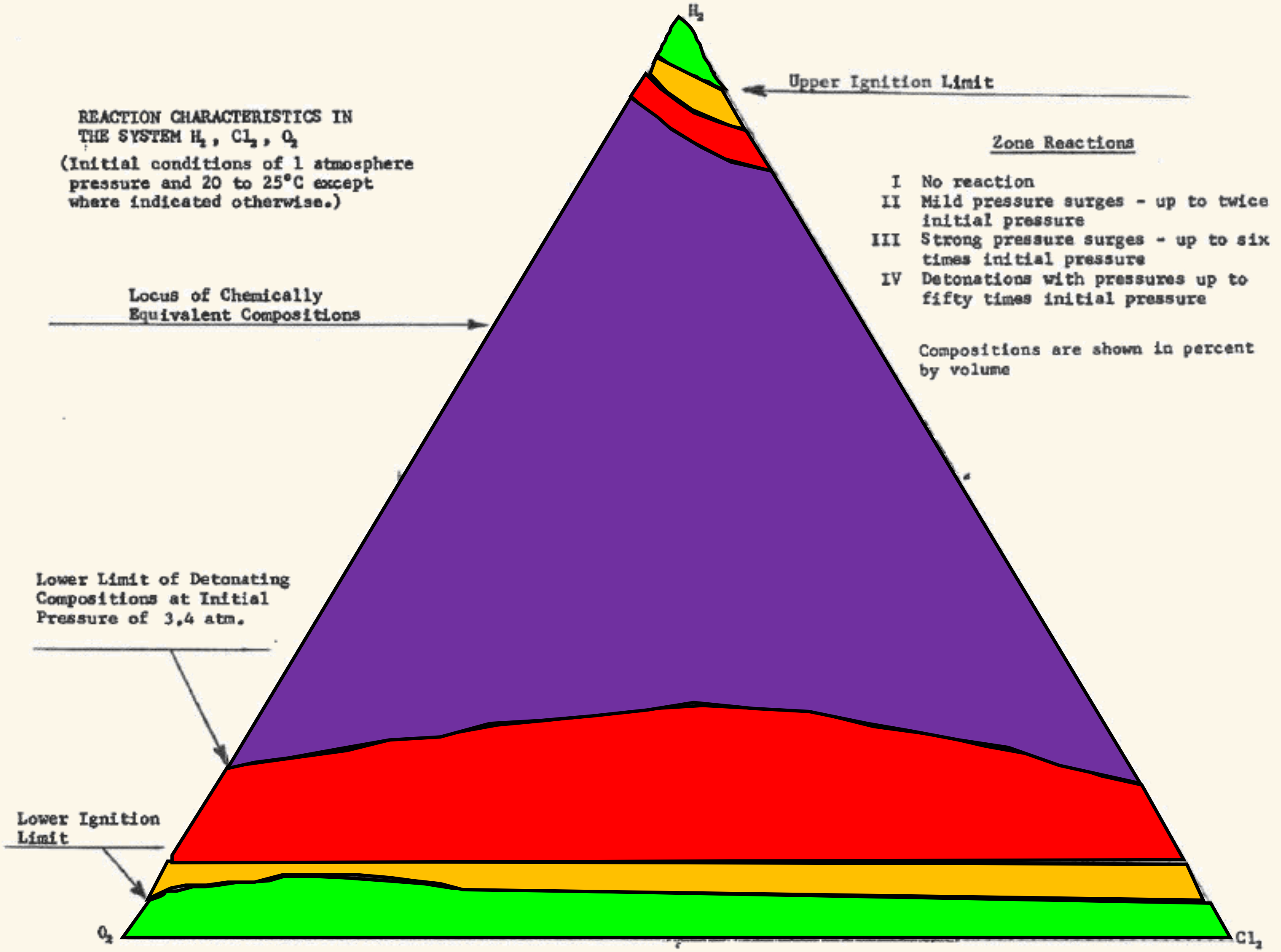
- The explosion limits are defined as an increase of 5% of the initial pressure after ignition by an ignition source
- Data:

Temp. in °C	H_2 - Air (vol% H_2)	H_2 - O_2 (vol% H_2)	H_2 - Cl_2 (vol% H_2)
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
20 - 25	4.0 - 75	4.0 - 96	3.0 - 92.5
50	3.7 - 76	4.0 - 96	3.0 - 93

- Depending upon the temperature: 3.0 – 4.0 vol%
- Explosion increases the pressure <u>and</u> temperature → Initiates Chlorine-Iron fire?
- Detonation: pressure can increase 50-fold

Lower explosion limit (LEL)

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



Hydrogen in anolyte side of electrolysers

- Sources of hydrogen:
  - Diffusion of hydrogen through membrane to anolyte side driven by concentration difference
  - Transport of hydrogen through pinholes in membrane to anolyte side due to:
    - aging
    - history of process conditions being outside operating window affecting the mechanical integrity of the membrane
  - Metal parts in the inlet and outlet hoses of the anode compartment acting as cathode and producing hydrogen due to leak-currents or stray-currents (depending upon cell technology)
- Several failure scenarios resulting in increase of hydrogen concentration in chlorine gas from electrolysers
- UV light passing through the wall of hoses of membrane technology can be ignition source. Also starting the flow of brine or catholyte can cause ignition

Hydrogen production in the electrolyser and headers

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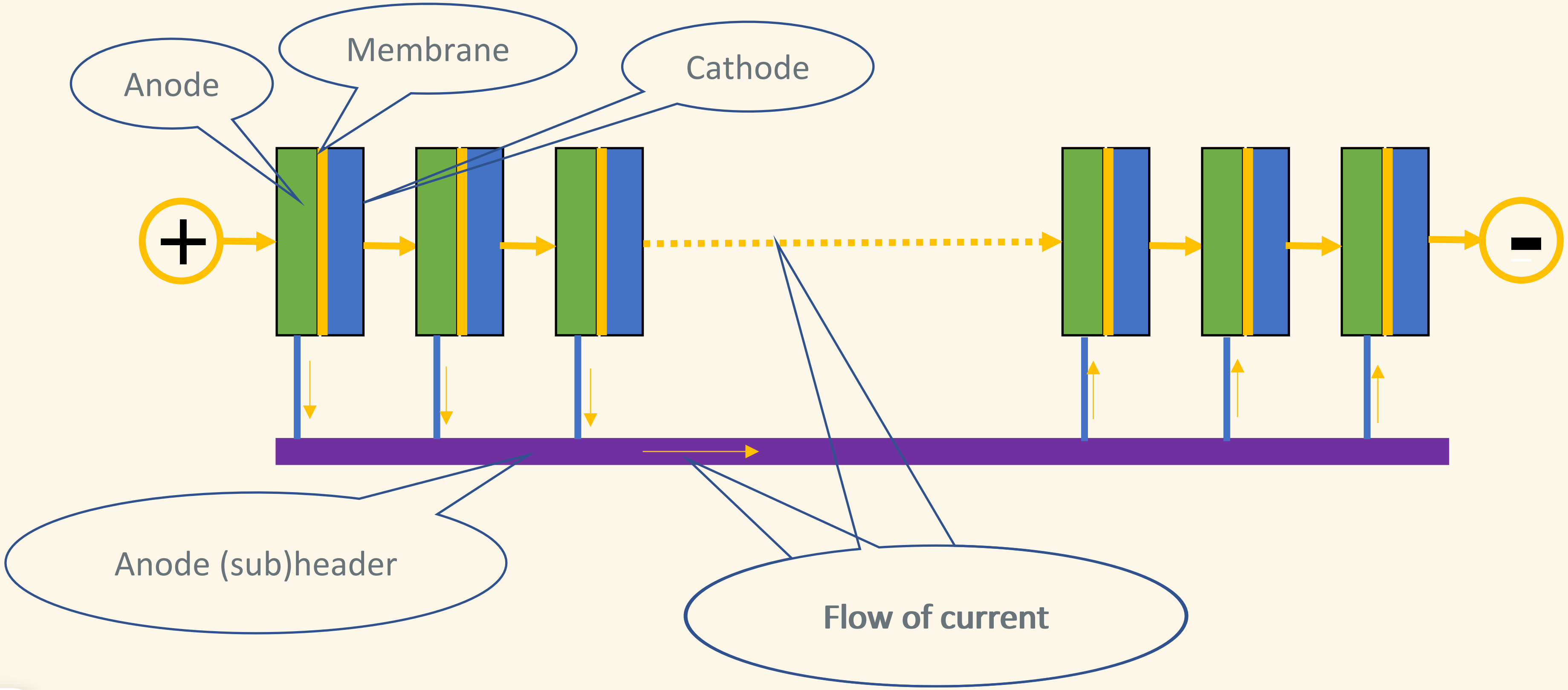
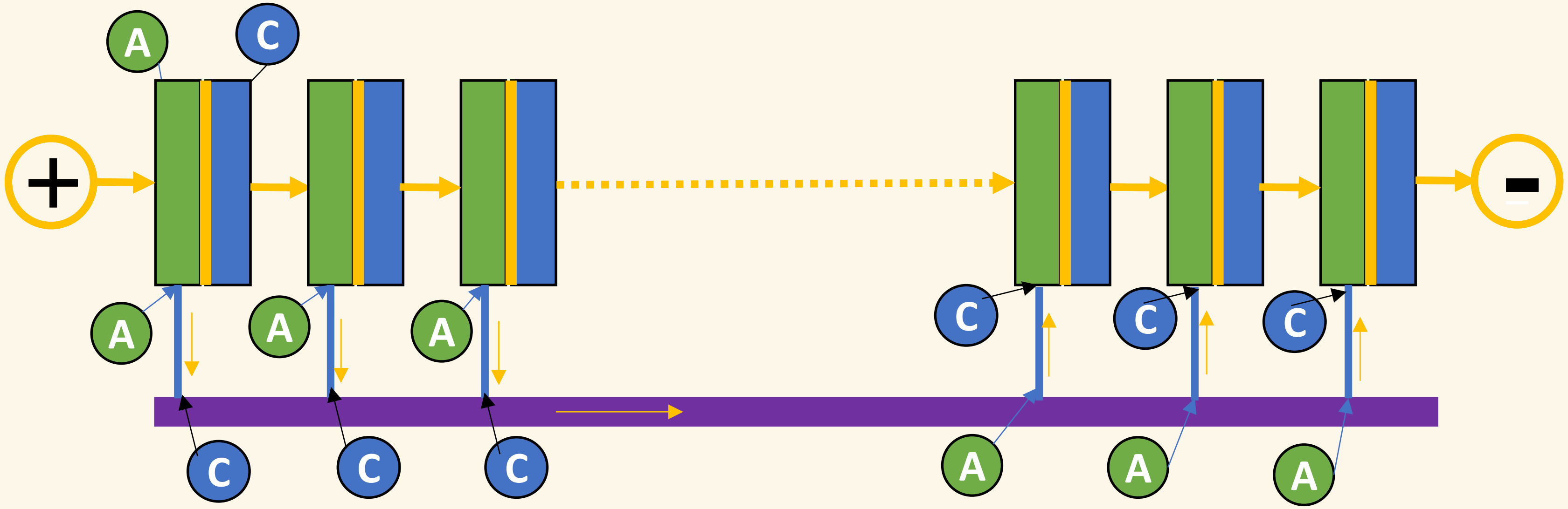
- Via shunt-current, by-pass current or stray current
- An electrolyser contains several cells that are all connected to headers, these connections and headers contain conducting liquids



Hydrogen production in the electrolyser and the headers

- Metal parts in the (sub)headers and hose connections will act depending on their position as anode or cathode



- On the cathodes H_2 will be produced resulting in H_2 in chlorine
- Amount depends mainly on the electrolyser voltage and the electrical resistance of the anolyte connections, (sub)headers and metal area acting as a cathode

Normal operation of electrolysis

- Electrolyser producing chlorine
  - Technical state of membrane and pressure difference determines the mass flow of hydrogen to the anolyte side
  - The actual chlorine production determines the hydrogen concentration
  - The actual chlorine production determines the oxygen formation
  - Typical concentrations in chlorine gas on dry basis:

Component	Concentration
O_2	0.3 – 2.0 vol%
H_2	0.01 – 0.1 vol% 1)
N_2	Normally not present

In zero gap technologies the hydrogen concentration is roughly twice as high compared to finite gap technologies as stated above
0.3 vol% O_2 can be reached only in case of brine acidification

  - 40 – 60 vol% H_2O in gas from cell room: LEL of H_2 is 5 – 7 vol%

Normal operation of electrolysis (cont'd)

- Startup of an electrolyser
  - If applicable: during polarization an explosive mixture of hydrogen and oxygen can be formed at the anolyte side
  - Inevitably the chlorine production is low, hence the potential hydrogen concentration is high
  - Ignition sources: sunlight (via hoses), start of supply of electrolytes
  - Securing safe hydrogen concentration:
    - Purge the Cl_2 and H_2 electrolyser sub-headers with nitrogen (prior to start-up and polarization (if applicable))
    - Fast increase of the current on the electrolyser for fast reduction of the H_2 concentration by Cl_2 produced. Ramp rate should not exceed the maximum for the cell voltage measurement and safeguarding system
    - Continue to purge the chlorine sub-header with nitrogen until H_2 level in the sub-header of this electrolyser is sufficiently low

Normal operation of electrolysis (cont'd)

- Shutdown of an electrolyser
  - Inevitably the chlorine production is low, hence the potential hydrogen concentration is high
  - After reducing the current to zero the liquid level on the anolyte side and on the catholyte side drop (zero gas fraction) and a part of the membrane is exposed to gas on both sides causing more flow of H_2 through the membrane until the level on the catholyte side has increased to the top of the cell.
  - If applicable: during polarization an explosive mixture of hydrogen and oxygen can be formed at the anolyte side
  - Securing safe hydrogen concentration:
    - Continuing flow immediately after reducing current to zero reduces the area exposed to gas on both sides and minimizes the transport of hydrogen to the anolyte side
    - Purge H_2 und Cl_2 header with nitrogen to prevent an explosive atmosphere built-up in a header or even further downstream.
    - Limit the duration of this process state: transport of H_2 to anolyte side continues, polarization unit causes production of H_2

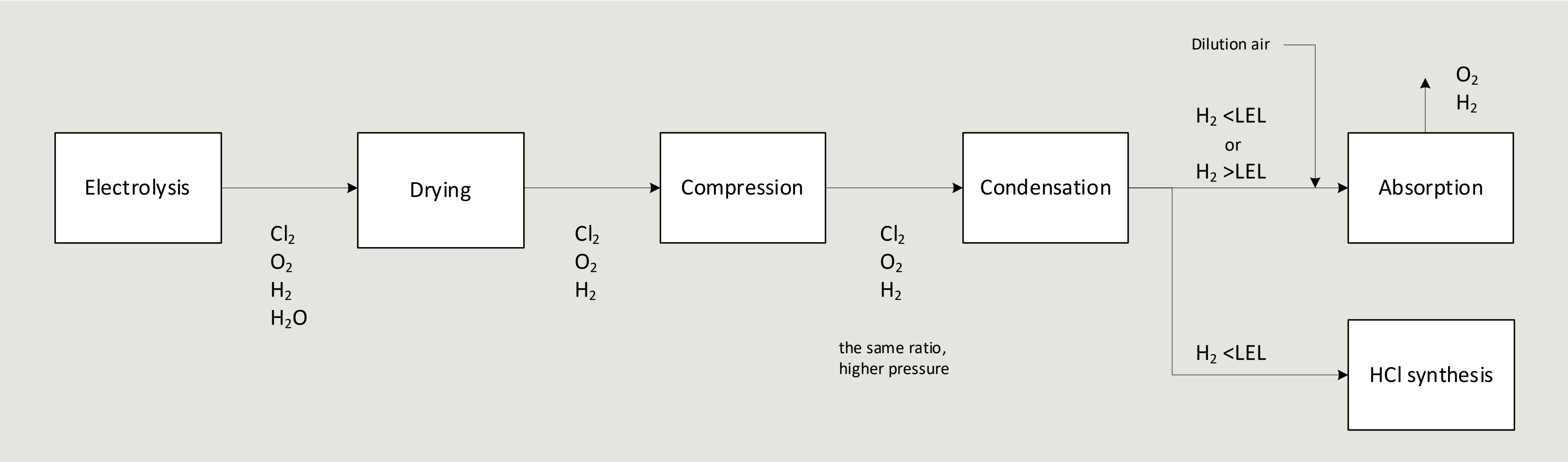
Normal operation of downstream processing

- Gas from cells contain max. 40.0 – 60.0 vol% of H_2O (1 – 2 bara, max. 90°C)
- Drying:
  - Removal of water
  - Hydrogen concentration after drying is far below the LEL
- Compression:
  - Without a recycle from downstream condensation the hydrogen concentration remains unchanged
  - Up to 13 bara the LEL in Cl_2/H_2 mixture is 3.0 vol%

Normal operation of downstream processing (cont'd)

- Condensation:
  - Hydrogen in tail gas
    - Concentration < LEL
    - Concentration > LEL → Robustness of the mechanical design
  - Securing safe operation:
    - Measure and control H_2 concentration in streams with concentration < LEL
    - Correcting variables:
      - Flow of tail gas
      - Flow of nitrogen supply
- Destination of tail gas:
  - HCl synthesis: its burner is a potential ignition source
  - Chlorine absorption: Safe operation requires sufficient dilution with air or nitrogen
    Chlorine is absorbed, water vapor condenses: LEL in air is higher than in chlorine: 4.0 vol%

Hydrogen from electrolysis to downstream processing



Normal operation

Start-up / Shutdown

Failure scenarios

Failure scenarios electrolysis and how to reduce risk

- Process conditions outside the operating window of the membrane causing severe damage (pinholes or tears in membranes):
  - Blocked brine and/or catholyte flow leads to high voltage, causing high temperature and possible failure of membrane;
  - High temperature due to failing temperature control;
  - Wrong anolyte or catholyte concentrations due to failure of concentration control;
  - High or low differential pressure due to failure of differential pressure control;
  - Over acidification due to failure of acidity (pH) control
- Dilution:
  - More hydrogen from a few cells diluted by chlorine gas from undamaged cells
  - More hydrogen from one electrolyser diluted by chlorine gas from undamaged electrolysers
- During production, but also during startup and shutdown

Failure scenarios electrolysis and how to reduce risk (cont'd)

- Reducing the frequency by:
  - Membrane leak test before startup
  - Reliable control loops
  - Safety instrumented functions with the following initiators:
    - Temperature
    - Pressure, pressure difference
    - Flow of brine, flow of catholyte
    - Cell voltage monitoring and safeguarding system:
      - Measures voltage of all individual bipolar cell elements of a membrane plant
      - Voltage profile test: pinhole detection during shutdown and startup
      - Difference between average voltage of the complete electrolyser and individual cell voltage. This can trip the electrolyser in an early stage, for example when brine feed to one element is blocked.
      - Low voltage: severe membrane damage or short-circuit
    - H_2 concentration in subheader

Failure scenarios for condensation and how to reduce risk

- Causes:
  - Higher H_2 concentration in gas from cell room
  - Reduced flow of tail gas due to:
    - Flow control of tail gas failing low
    - H_2 concentration control failing high
    - Temperature control of tail gas failing low
- Reducing the risk frequency by:
  - Ensure a minimum flow of tail gas via bypass flow control valve of tail gas
  - Safety instrumented function:
    - Initiator: H_2 concentration in tail gas
    - Final elements:
      - opening tail gas control valve, or increase condensation temperature
      - adding N_2 or air to dilute H_2
      - Stopping electrolysis

Online Hydrogen concentration measurement

- Infrared spectrometry:
  - Hydrogen in sample gas is thermally converted to HCl → flame arrestor to protect against ignition
  - Measuring the HCl concentration of resulting sample gas
  - Fast
- Thermal conductivity:
  - The thermal conductivity of hydrogen is much higher than the thermal conductivity of chlorine and oxygen → flame arrestor to protect against ignition
  - Sample gas is split in two streams: One stream passes a UV reactor or quartz oven to convert all H_2 with Cl_2 or O_2
  - Measuring the difference of thermal conductivity between these two streams

Online Hydrogen concentration measurement

- Gas chromatography
  - Allows simultaneous determination of other components presents in the chlorine gas (oxygen, nitrogen and carbon dioxide)
  - Measurement time is slow, and the complete system design is complex

- TDLAS: Tunable Diode Laser Absorption Spectroscopy
  - Direct measurement of hydrogen in the chlorine gas.
  - The measurement is very specific with fast measurement times and low complexity
  - But the precision is lower compared to the other methods.

Occurrences of hydrogen explosions

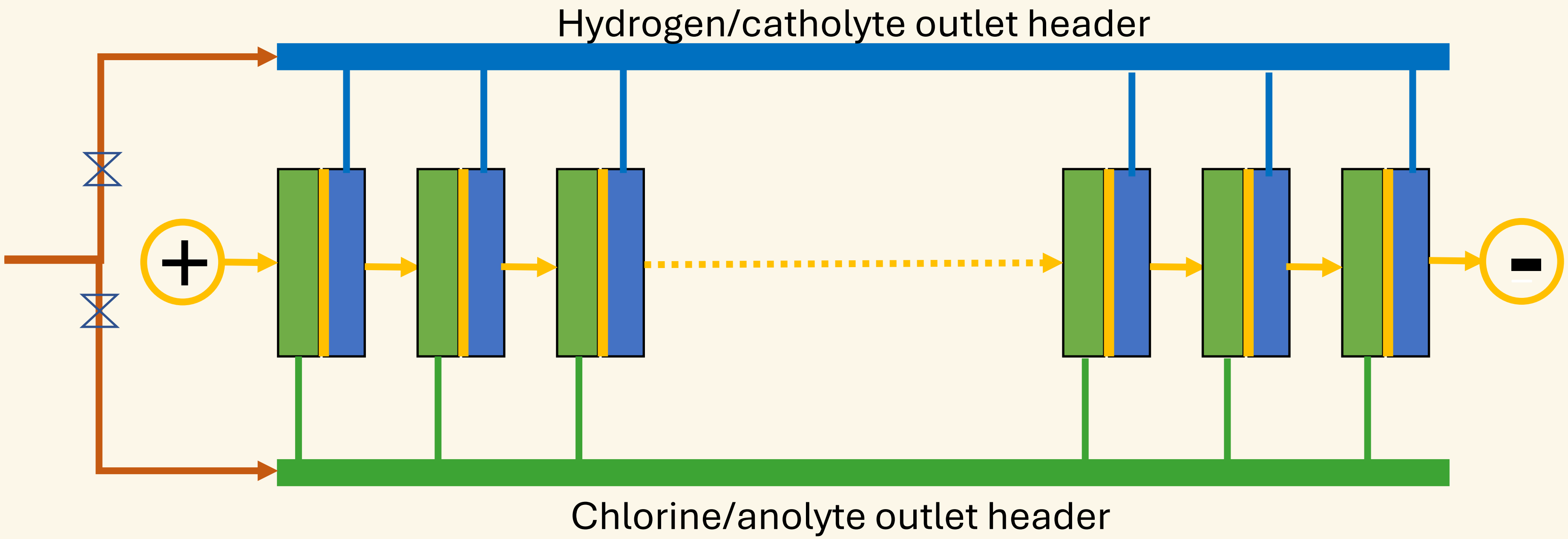
- In the cell (an electrolyser with a few damaged membranes): loss of containment is usually limited to a few damaged cells or gaskets blown out
- Chlorine drying: high probability of ignition due to static charging of sulfuric acid (conductive liquid) in a column made of (non-conductive) plastic resulting in loss of containment
- Liquefaction: probability of ignition is low unless a source is present, such as an online hydrogen analyser (hot surface or UV reactor) with a failing flame arrestor in the sample gas line or a hotspot

Example of explosion:

- Explosion in Cl_2 electrolyser sub-header and (somewhat later) chlorine cooler
- Resulting in damaged membranes and electrodes in electrolyser
- No other equipment damaged

Example of explosion (cont'd)

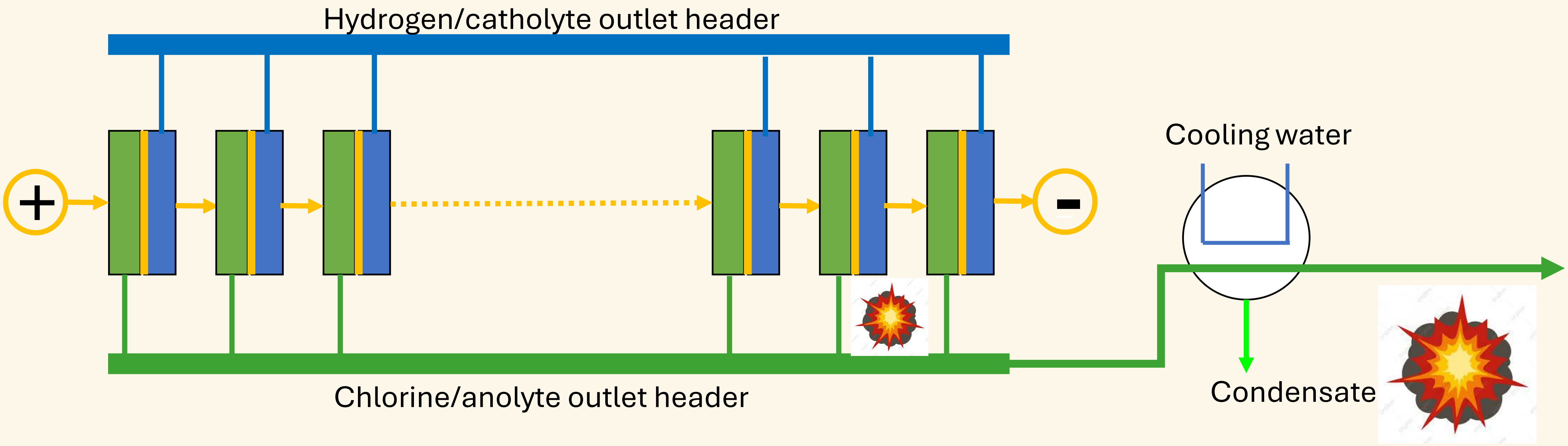
- What happened?



- Before start-up the electrolyser was pressurised with N_2
- The electrolyser was energised

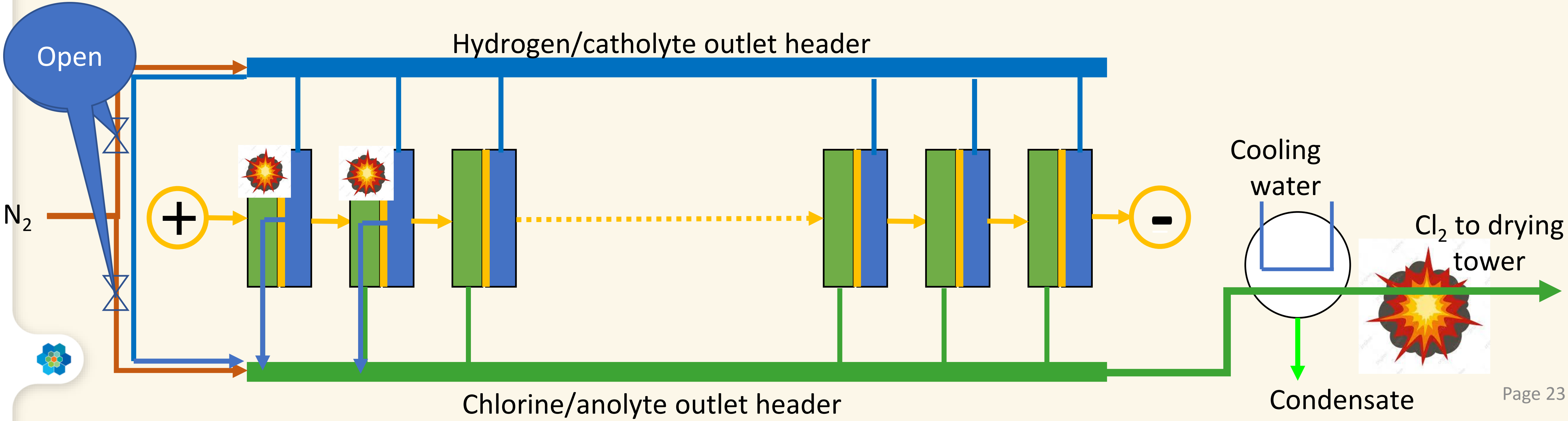
Example of explosion (cont'd)

- A small explosion took place in the anolyte electrolyser header (not noticed)
- Some time later a larger explosion took place in the chlorine coolers



Example of explosion (cont'd)

- After pressurising, the nitrogen valves were not closed
- After energising, H_2 could flow from catholyte header to anolyte header
- Resulting in a small explosion, damaging membranes
- Resulting in a larger flow of hydrogen
- Resulting in the explosion in the coolers



Example of explosion (cont'd)

Root cause?

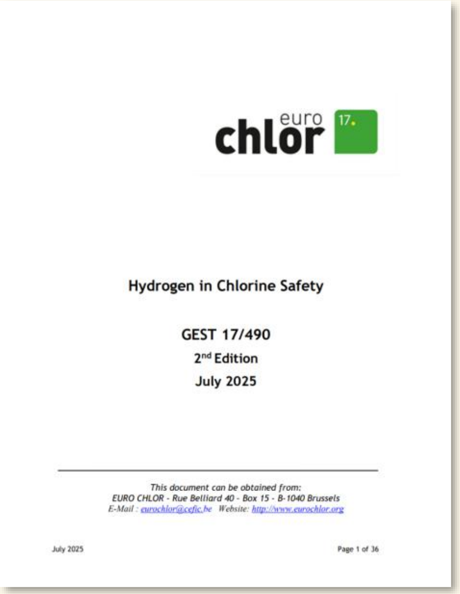
- Neglecting the operating procedure of closure of the N_2 valves

Options to improve:

- Add check valves in the nitrogen to the anolyte and catholyte header
- Make use of the voltage monitoring system
- Install H_2 measurement at each electrolyser and/or in central chlorine header

Reference documents

- GEST 17/490, Hydrogen in Chlorine safety, 2nd Edition, July 2025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Hydrogen in Chlorine Safety

GEST 17/490
2^{nd} Edition
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EURO CHLOR - Rue Belliard 40 - Box 15 - B-1040 Brussels
E-Mail : eurochlor@cefic.be Website: http://www.eurochlor.org

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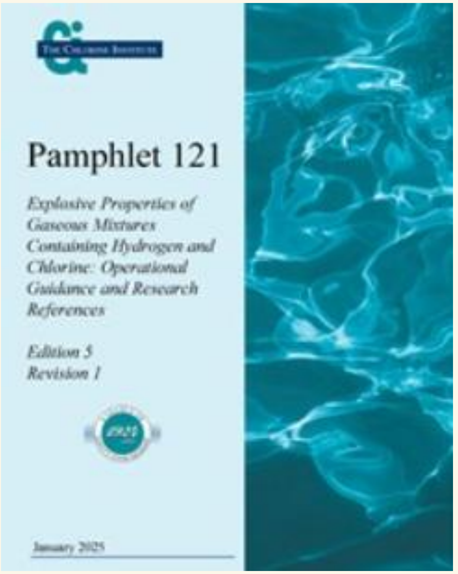
- Pamphlet 121) Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine


Pamphlet 121

Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine: Operational Guidance and Research References

Edition 5
Revision 1

THANK YOU

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