



HCL SYNTHESIS UNITS WITH ENHANCED SAFETY FEATURES






CLOSUR NOVEMBER 2016



MERSEN: WHO ARE WE?

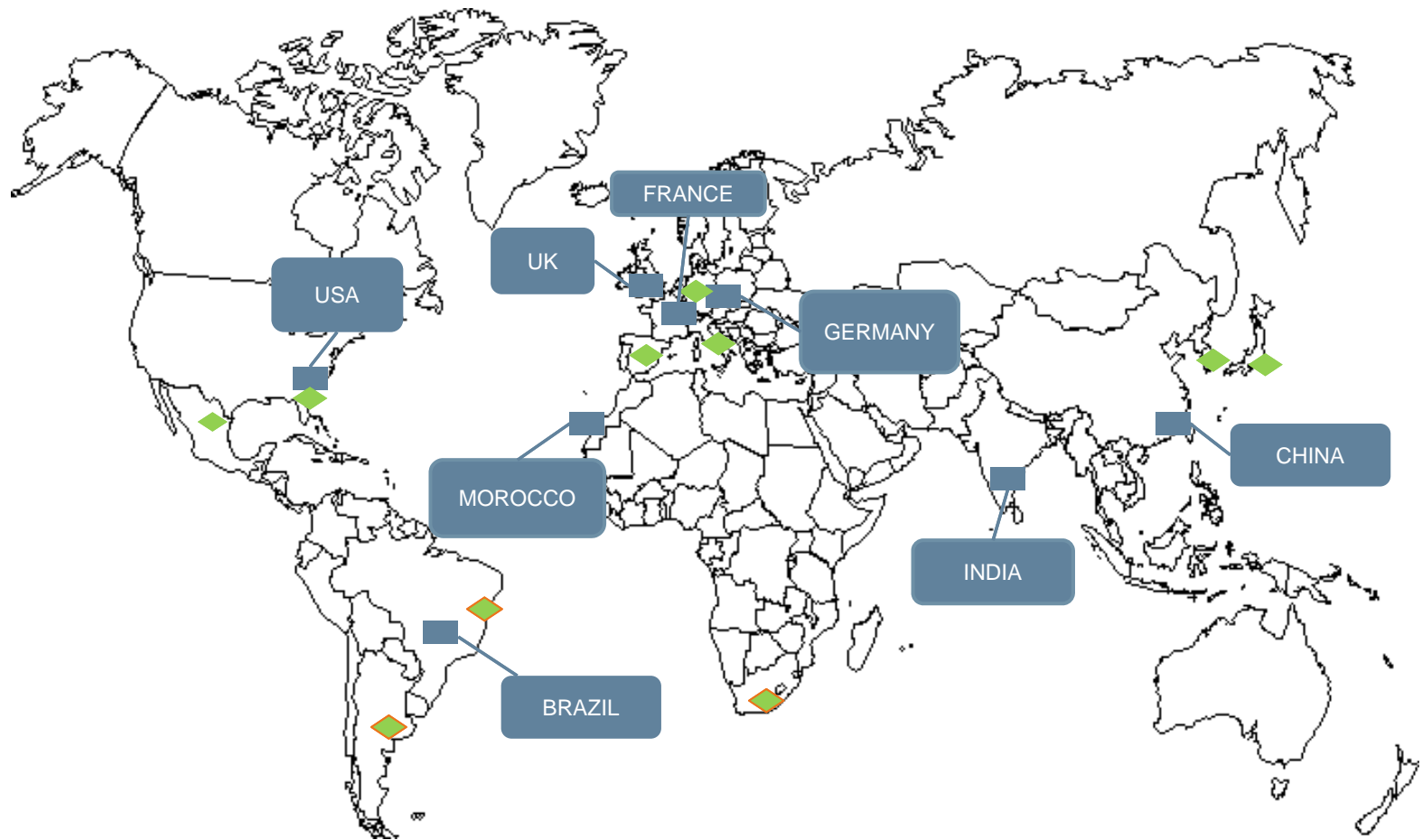
AN INDUSTRIAL BASED COMPANY SUPPLYING EQUIPMENT & KNOW HOW TO OUR CLIENTS

TWO MAIN SUBDIVISIONS- PRODUCT FOCUS AREAS

<i>ADVANCED MATERIALS</i>	<i>ELECTRICAL POWER</i>
ANTICORROSION EQUIPMENT 	ELECTRICAL PROTECTION & CONTROL 
GRAPHITE SPECIALTIES 	SOLUTIONS FOR POWER MANAGEMENT 
POWER TRANSFER TECHNOLOGIES 	

2015 Group Sales of ~\$850 million
~7000 employees world wide

MERSEN: WHERE WE ARE...



- Production sites:
- ◆ Quick Center

MERSEN ANTICORROSION AND PROCESS EQUIPMENT

IDEALLY SUITED FOR THE CHLOR-ALKALI INDUSTRY



- **DESIGN AND MANUFACTURE OF PROCESS EQUIPMENT :**
 - Heat exchangers, pressure vessels, mixers, columns
 - Engineered skid packaged systems
 - Piping, fittings
- **IN A WIDE RANGE OF MATERIALS**
 - Graphite, SiC
 - Tantalum, zirconium
 - Titanium
 - Nickel alloys
 - PTFE, PFA
 - Carbon steel, stainless steel
- **FOR CORROSIVE APPLICATIONS IN PROCESS INDUSTRIES**
 - Chemicals, Fine chemicals, pharmaceuticals
 - Hydrometallurgy & pickling
 - Agrochemical & Water treatment



MERSEN ANTICORROSION AND PROCESS EQUIPMENT

PRODUCTS IDEALLY SUITED FOR THE CHLOR-ALKALI INDUSTRY

- Graphite equipment for transformation of HCl acid and gas (heat exchangers, **synthesis units**)
- Titanium wet Cl₂ coolers & demisters
- Titanium piping
- Titanium brine heaters
- Titanium reactors & tanks for hypochlorite (bleach)
- Nickel 200 coolers & heaters for NaOH
- PTFE piping for wet Cl₂ and HCl



MERSEN ANTICORROSION AND PROCESS EQUIPMENT SYSTEMS OFFERED FOR THE CHLOR-ALKALI INDUSTRY

- HCl synthesis units
- brine treatment
- H₂SO₄ dilution & concentration
-
- Cl₂ recovery (stripping) from brine solutions
- Plants for PAC (PolyAluminum Chloride)
- Plants for FeCl₃



PROCESS FUNCTION	H ₂ SO ₄	HCl	Cl ₂	HBr	Br ₂	P ₂ O ₅	Brine	Flue Gas	FeCl ₃
Absorption		✓		✓				✓	
Burner		✓	✓	✓	✓				
Concentration	✓	✓		✓		✓			✓
Dilution	✓	✓		✓		✓			
Gas Drying		✓	✓	✓					
Distillation/ Desorption/Stripping		✓	✓	✓					
Gas cleaning / Vent treatment		✓	✓	✓	✓			✓	
Inorganic removal	✓	✓				✓	✓		✓
Organic removal	✓	✓		✓		✓	✓		✓
Production		✓		✓	✓				✓
Temp. Control	✓	✓		✓		✓		✓	
Vaporizer		✓	✓	✓	✓				
Vacuum system	✓	✓	✓	✓		✓	✓		✓

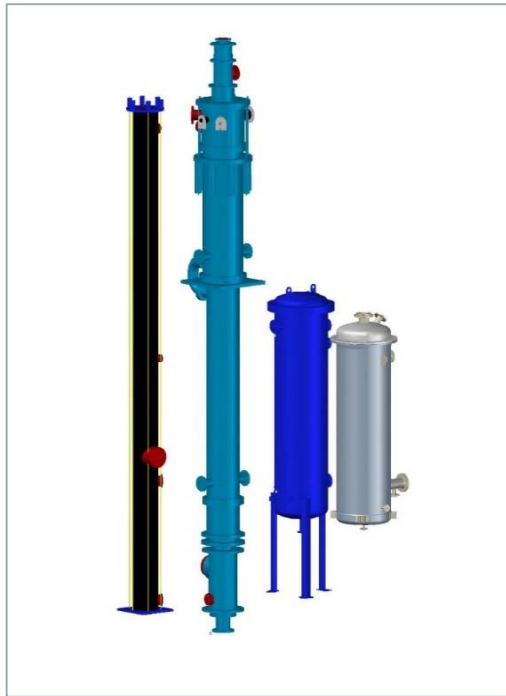
Enhanced safety for HCL synthesis units

MERSEN TECHNOLOGY

MERSEN IS A WORLD LEADER FOR THE SUPPLY OF HCL SYNTHESIS UNITS WITH OVER 600 UNITS INSTALLED PROVIDING A TOTAL PACKAGE SOLUTION

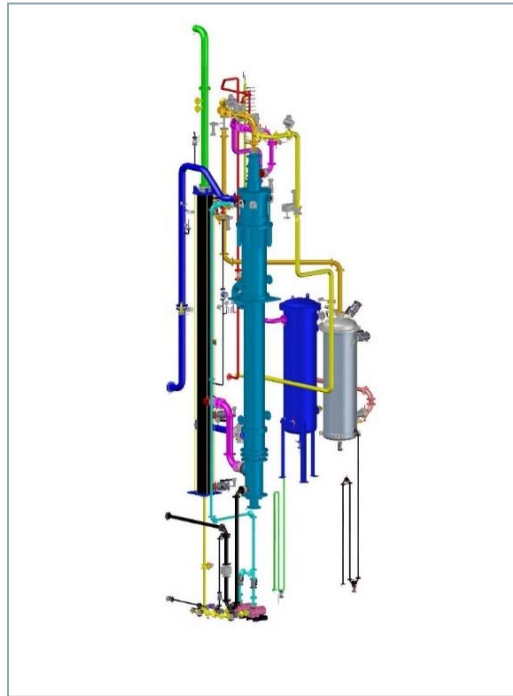
■ ENGINEERING

- Conceptual design
- P&ID
- Basic/detail engineering
- Main equipment supply



■ PROCUREMENT

- Instrumentation
- Piping and valves
- Automated control cabinet
- Main equipment supply



■ CONSTRUCTION

- Main equipment supply
- Modular assembly includes: the installation of steel structure, equipment, piping & valves, instrumentation, cabling, junctions boxes

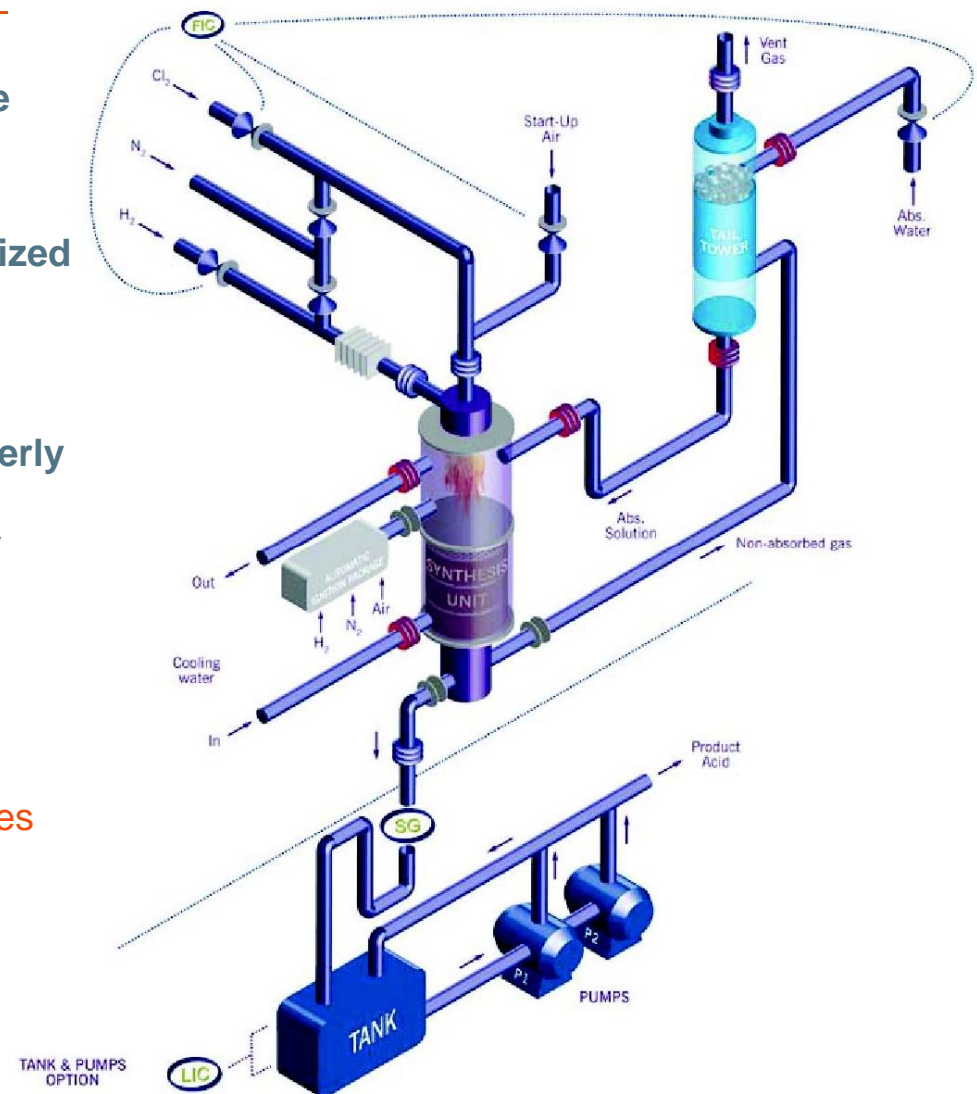


→ Skid-mounted turn-key solution

Enhanced safety for HCL synthesis units

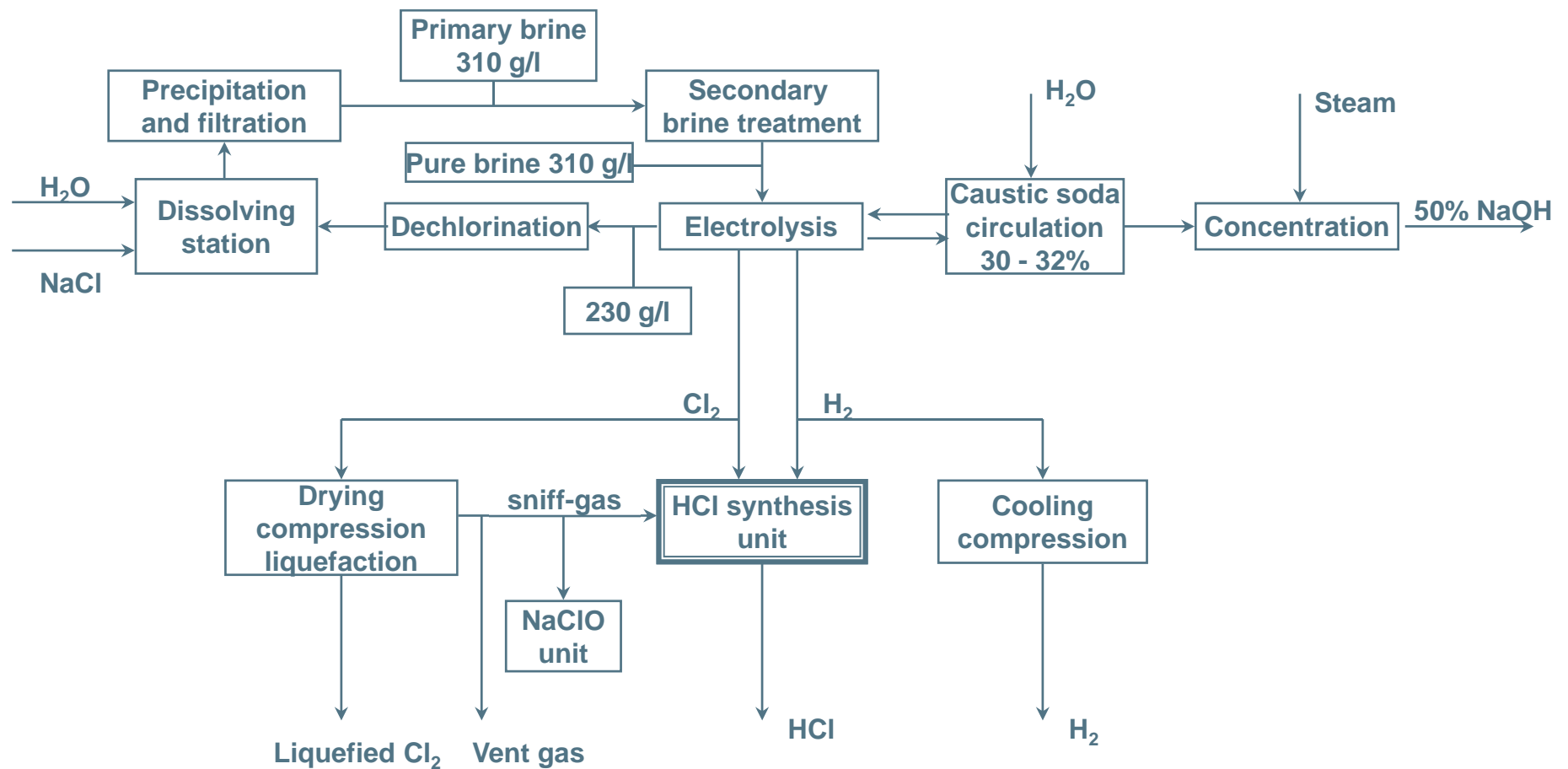
MERSEN TECHNOLOGY

- Hydrogen chloride is formed by burning chlorine with a slight excess of hydrogen.
- $\text{Cl}_2 (\text{g}) + \text{H}_2 (\text{g}) \Rightarrow 2 \text{HCl} (\text{g}) + 600 \text{ kcal/kg}$
- Hydrogen chloride gas is absorbed in demineralized water to form pure hydrochloric acid.
- This is a combustion process involving a very reactive mixture of gases which can, if not properly managed, cause an explosion and cause major property damage and personnel injury or fatality
- **MERSEN safety enhancements**
 - Material selection
 - Safe equipment design
 - Attention to control philosophy and safe practices (HAZOP/LOPA, etc.)
 - Process control & selection of control elements
 - BMS- Burner Management System



HCL synthesis units – 95% of the world's units are connected to a Chlor-Alkali plant

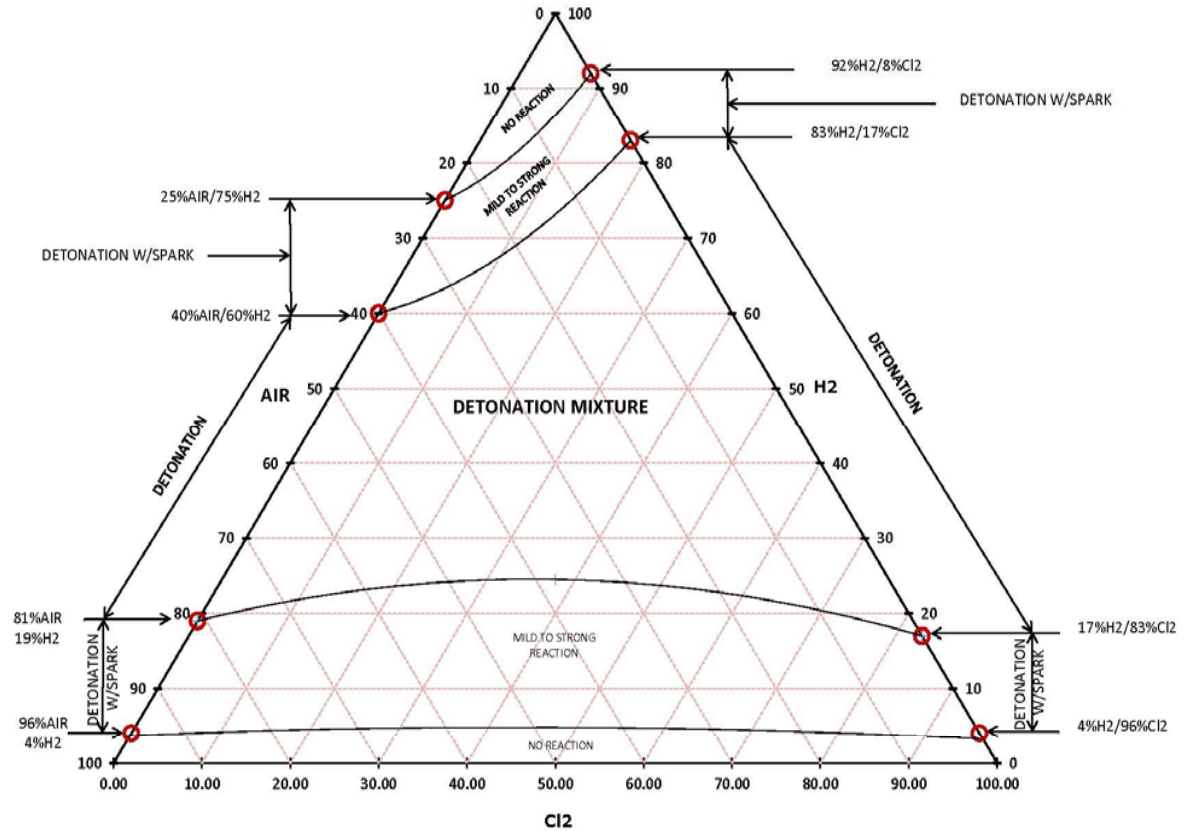
THE MEMBRANE ELECTROLYSIS PROCESS



Enhanced safety for HCL synthesis units

-explosion triangle

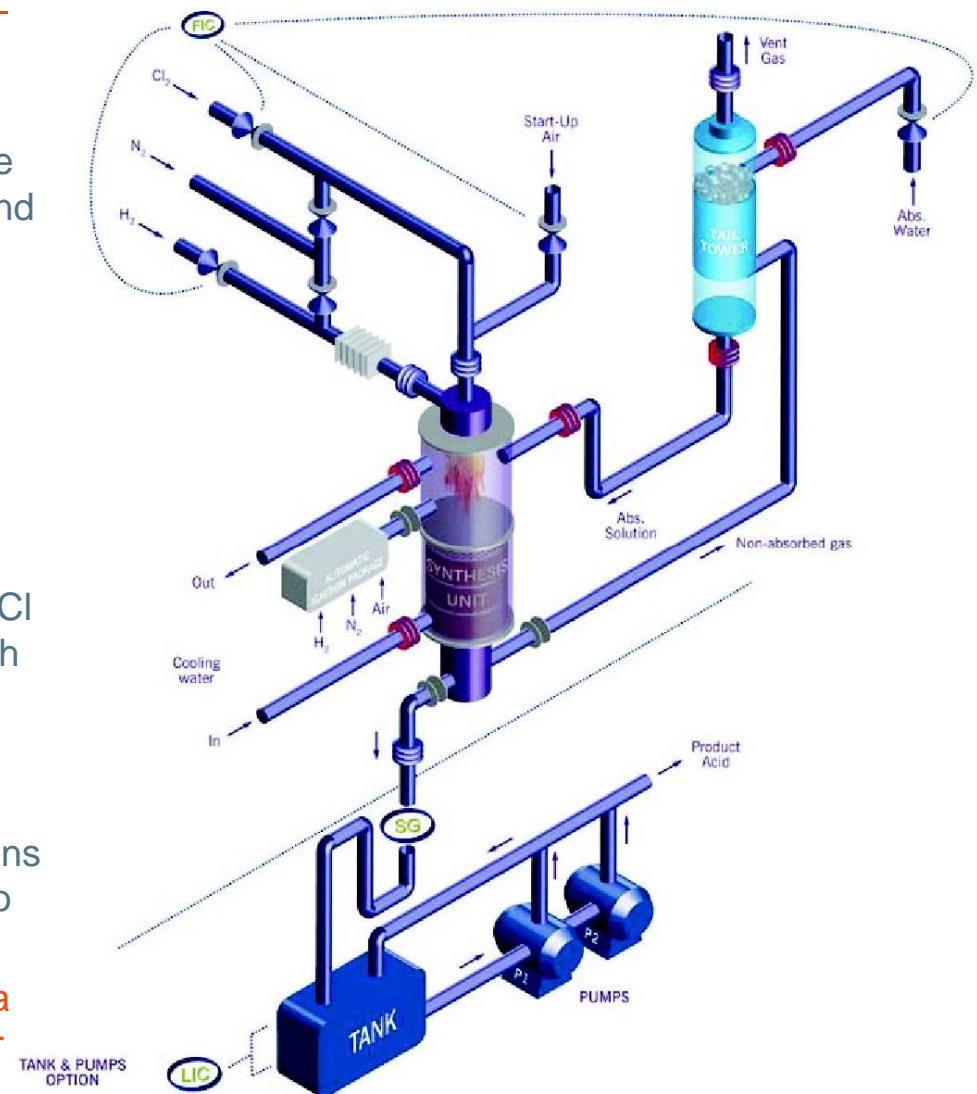
- **Biggest danger with any synthesis unit is an explosion of unburned gases**
- The explosion triangle for H₂, Cl₂ and air is not very forgiving
- The energy requirement to set off an explosion even in the mild to strong reaction area of the triangle is very small – less energy than that from a small fluorescent light bulb
- Sunlight and even the smallest static discharge can trigger a detonation



Enhanced safety for HCL synthesis units

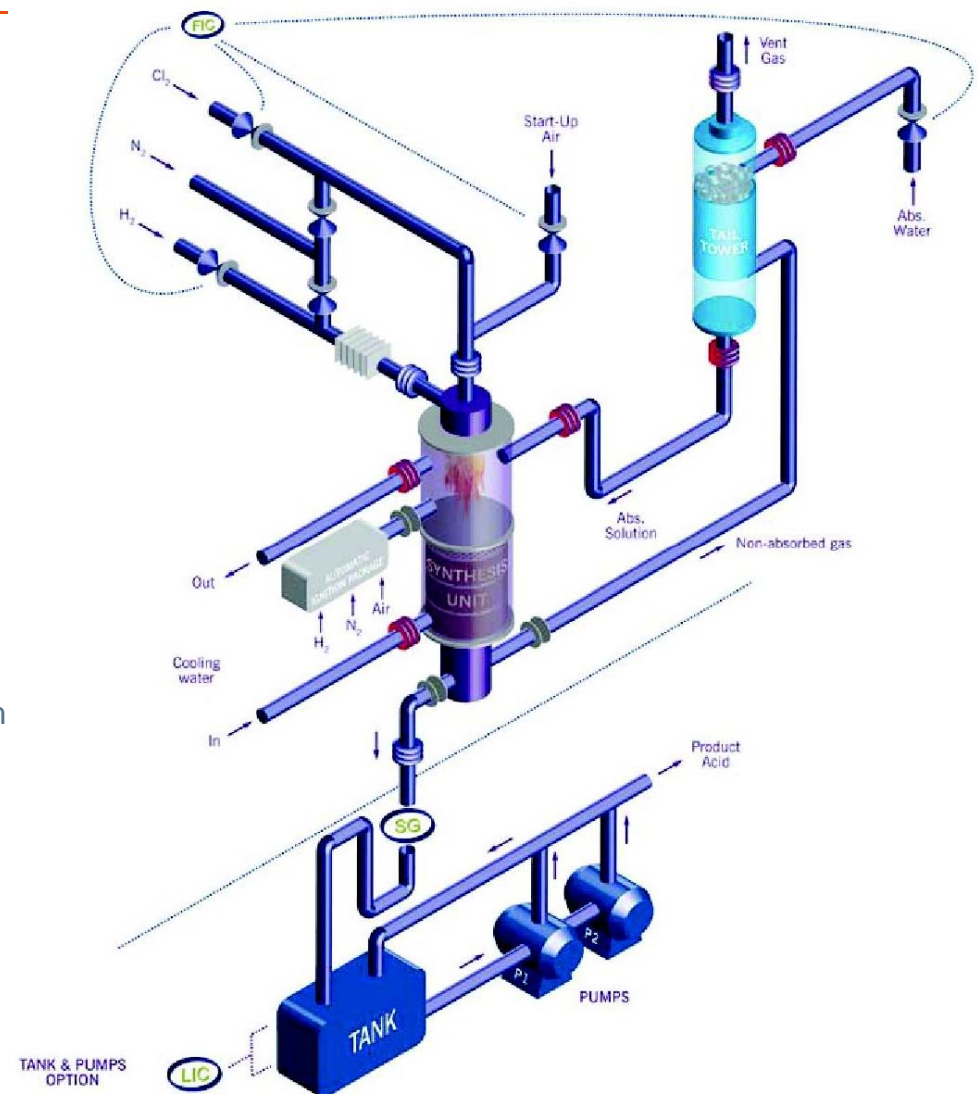
-crossing the stoichiometric boundary -1/2

- both the fuel (H₂) and an oxidant (Cl₂ or air) must be present for combustion (or an explosion) to occur and an ignition source must be present
- Normal operation: all of the oxidant (Cl₂) is carefully combusted in the burner chamber & furnace by operating with typically 10% excess fuel (H₂); stoichiometry is 1.1H₂/1.0Cl₂ (ratio of 1.1)
 - Near the burner, all of the Cl₂ is converted to HCl and what remains is typically ~95% HCl gas with ~5% excess H₂ and other inerts from the feed gas streams
 - After the absorption of HCl in water, what remains in the gas stream sent to the tail tower is 80% to 90%V H₂ with inerts
 - this is a danger zone if upsets occur or if a unit is controlled poorly and oxidant (air or additional Cl₂) is allowed to enter



Enhanced safety for HCL synthesis units- -crossing the stoichiometric boundary -2/2

- Dangerous conditions of unburned explosive gases can occur in a number of ways including:
 - Improper purging with N₂ at start up and shut down
 - A faulty start up sequence (with manual light up or auto-igniter)
 - Operating under vacuum (air can leak in)
 - Poor control during normal operation; crossing of the stoichiometric boundary
 - When the stoichiometric boundary of 1.0H₂/1.0Cl₂ is crossed to say 0.9H₂/1.0Cl₂ what remains near the burner is now ~95% HCl gas with ~5% excess Cl₂ and other inerts from the feed gas streams
 - After the absorption of HCl in water, what remains in the gas stream sent to the tail tower is 70% to 90%V Cl₂ with inerts;
 - **If the crossing occurs suddenly, a slug of Cl₂ can now meet with a slug of H₂ in the system and an explosion can occur and an emission of Cl₂ will also occur**
- **We will now discuss what MERSEN does to minimize these conditions**

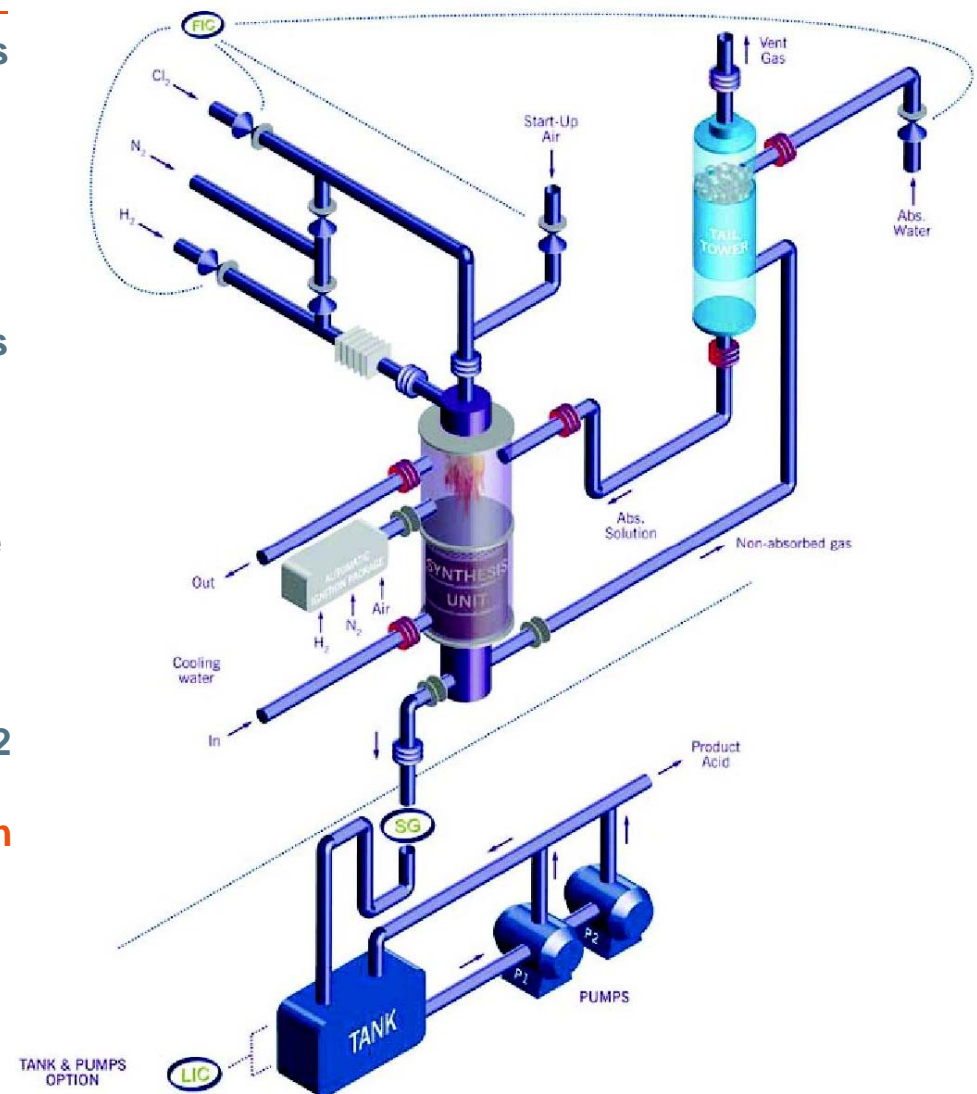


Enhanced safety for HCL synthesis units

MERSEN – Material Selection



- MERSEN Graphite material (named Graphilor 3®) is **conductive (non-sparking)**, highly corrosion resistant; it is composed of ultra fine grain isostatic graphite (<20µm) for **excellent mechanical resistance**.
- Graphilor 3® XC can withstand up to **430 deg C** ; it is used in high temperature areas --- **this provides additional safety if there is an upset**
- PTFE lined pipe (named ARMYLOR®) with graphite powder is **conductive material for anti-static protection**
- FRP equipment (like scrubbers or tanks) where H2 gas can be present use interior carbon veils (grounded to the exterior) **for anti-static protection**



Enhanced safety for HCL synthesis units

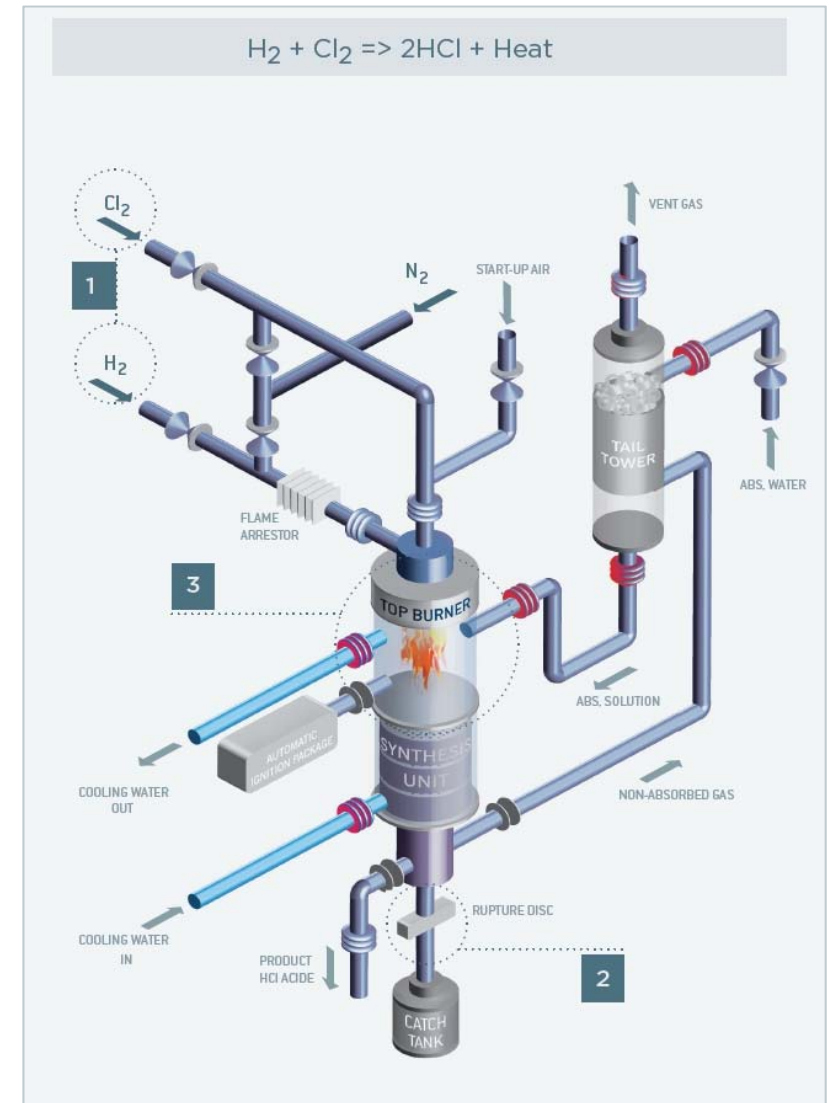
MERSEN design – top fired design



1. Burner + Reactor + Absorber encompassed in one piece of equipment
2. Wetted wall furnace design with optimized flame velocity & immediate liquid mass transfer (absorption) of acid permits reduced volume of gas in the unit
→ **translates to a reduced explosive volume & increased safety**
3. Hydrogen gas (volatile gas) & chlorine is far above the ground (above the pipe rack)
→ **ATEX area far above the ground.**
4. Chlorine gas is far above the ground (> 10 meters elevation).



Top firing technology = Best design for Safety

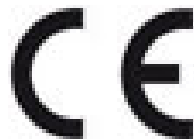
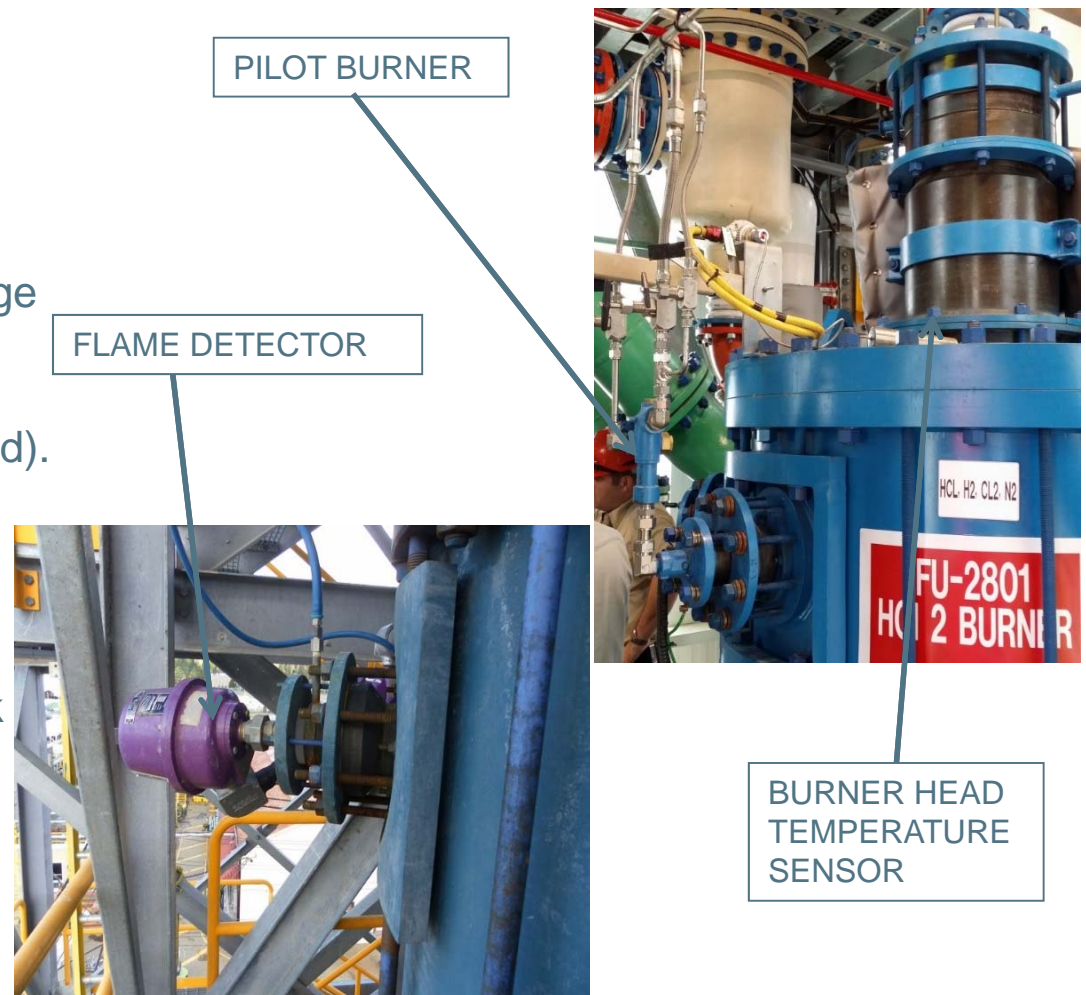


Enhanced safety for HCL synthesis units

MERSEN – safe design of ancillary devices and equipment 1/3



1. Flame detection (SIL3 & ATEX certified)
2. Rupture disc (in Graphilor 3®) with breakage detection – low pressure design.
3. Flame arrestor (ATEX & ISO-16852 certified).
4. Pilot burner (for automatic ignition) with integrated transformer
5. Burner head temperature sensor / interlock

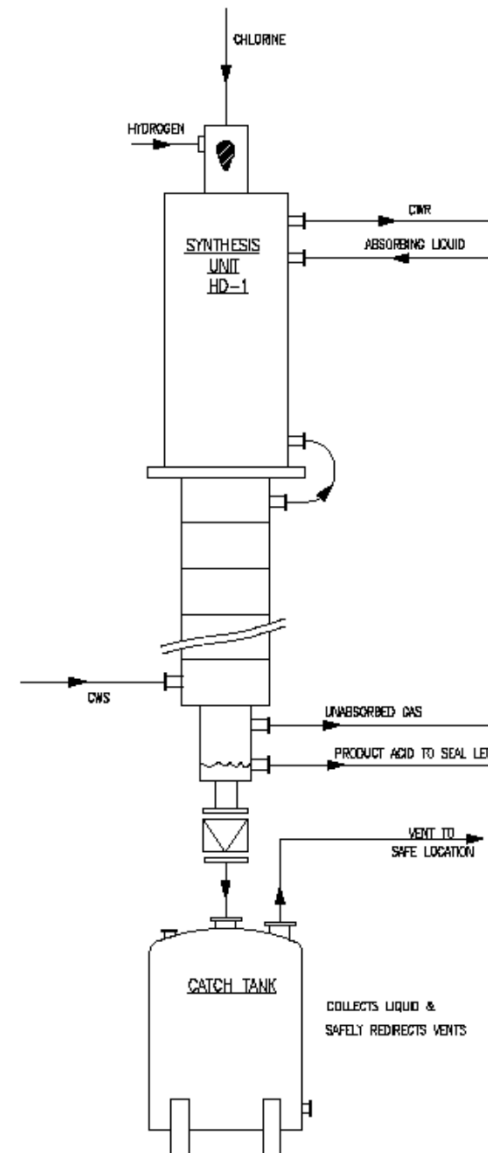


Enhanced safety for HCL synthesis units

MERSEN – safe design of ancillary devices and equipment 2/3



- Top fired means that a Catch Tank can be installed at the bottom to collect effluent when rupture disk breaks
 - Safely handles gaseous and liquid effluent
 - MERSEN's discharge of gas is typically less than 20% that of competitors that use an upfired design



Enhanced safety for HCL synthesis units

MERSEN – safe design of ancillary devices and equipment 3/3



- Double block & bleed on Hydrogen line.
- Positive pressure start up with an air combustion blower to avoid vacuum
- Flame extinguishment package on the stack
- Possibility to install caustic scrubber package for ultra-low emissions.
- Instrumentation package for safe start-up & operation (ATEX & SIL2 certified where possible)

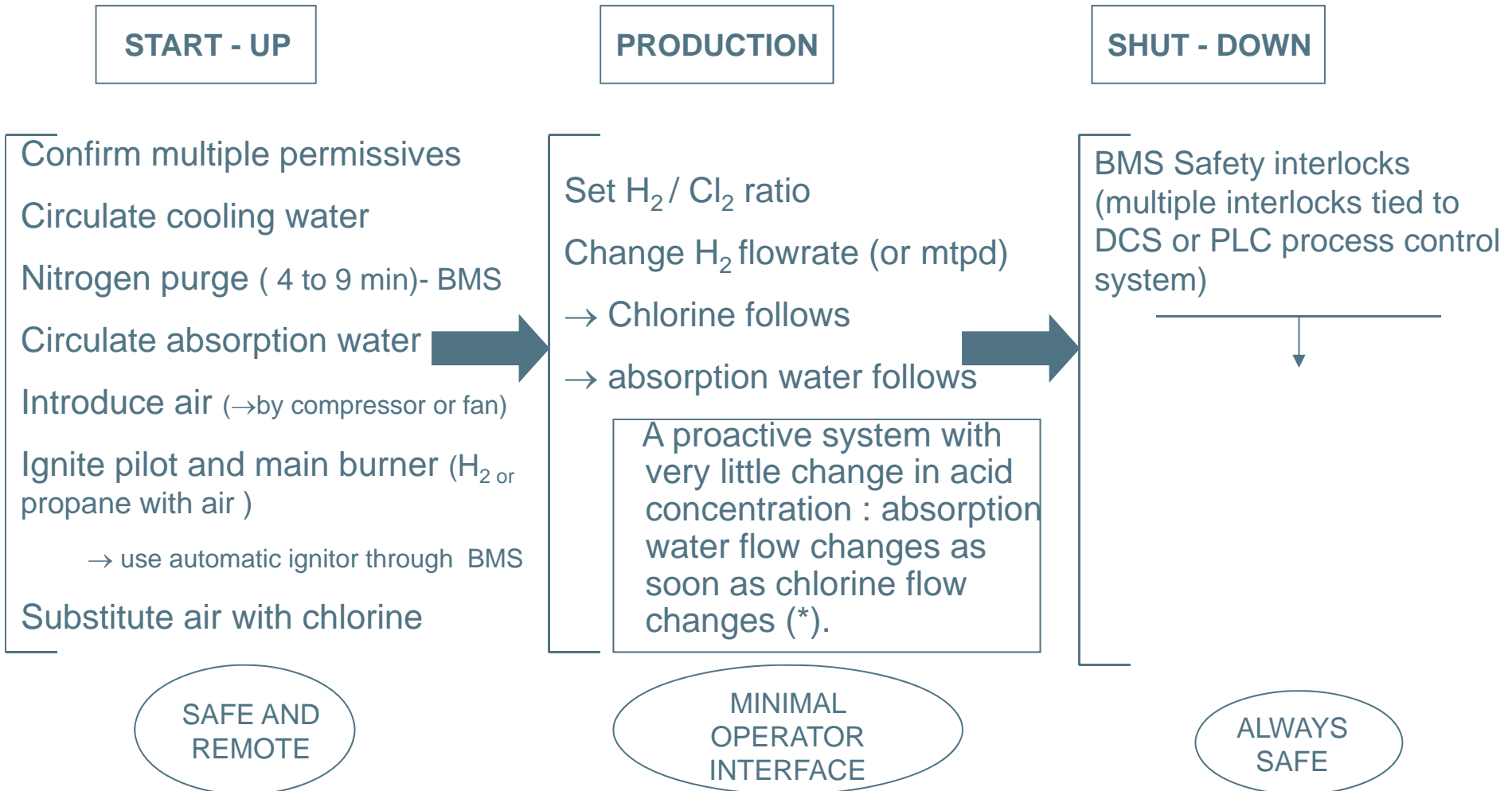


Enhanced safety for HCL synthesis units

MERSEN – control philosophy and HAZOP/ LOPA reviews



Careful attention must be given to the control philosophy including a safe start up of the unit.



(*) : for plants where chlorine purity varies , a %HCl concentration meter can be added to correct the absorption water flowrate.

Enhanced safety for HCl synthesis units

MERSEN – control philosophy and HAZOP/ LOPA reviews

- HAZOP or LOPA review meetings are a must for any new installation
- A HAZOP is only as good as the people participating in it
- MERSEN has over 600 units installed and has some of the most experienced engineers on the planet when it comes to the design, installation and operation of HCl synthesis units
- If you are installing MERSEN equipment or a MERSEN system, make sure you get MERSEN, with all its experience, participating in your HAZOP

Enhanced safety for HCL synthesis units

MERSEN – process control & selection of control elements



- Careful selection of the gas flow meters and control valves (for air, H₂ & Cl₂) are paramount for a good control system
 - Special consideration is required for the typical low pressure & corrosive feed conditions that prevail for most new systems that use low pressure gas direct from the electrolysis cells
 - In general, the higher the pressure drop across a meter or control valve the better the turn down and controllability
 - MERSEN carefully selects low dP meters and matches them to a suitable control valve that can handle all of the process conditions including start up transitions
 - Often pressure recovery meters (such as dP venturis) are used to better enhance controllability, especially for wet low pressure Cl₂
 - Control algorithms for the meters need to match accordingly



CL2 venturi dP flow meter

A. CHLORINE FLOW CALCULATION BASED ON DP FLOW (FIT-2801-42A) :

The flow for chlorine is calculated using the following formula in a reduced format:

$$Q_{Cl2 \text{ FIT-2801-42A}} = 1154.598 * Y * F_{TF \text{ TIT-2801-41}} * \text{SQRT} (P_{F \text{ PIT-2801-40}}) * \text{SQRT} (H_{W \text{ FIT-2801-42A}}) * (K_{MW \text{ AI-2801-48}}) \text{ scfh}$$

$$Q_{Cl2 \text{ FIT-2801-42A}} = \text{Corrected flow rate in scfh at } 60^{\circ}\text{F and 1 atmosphere}$$

$$Y (\epsilon) = \text{Expansibility factor (dimensionless)} \\ = 1 - 0.48143 * (1 - P_2/P_1)^{0.7407}$$

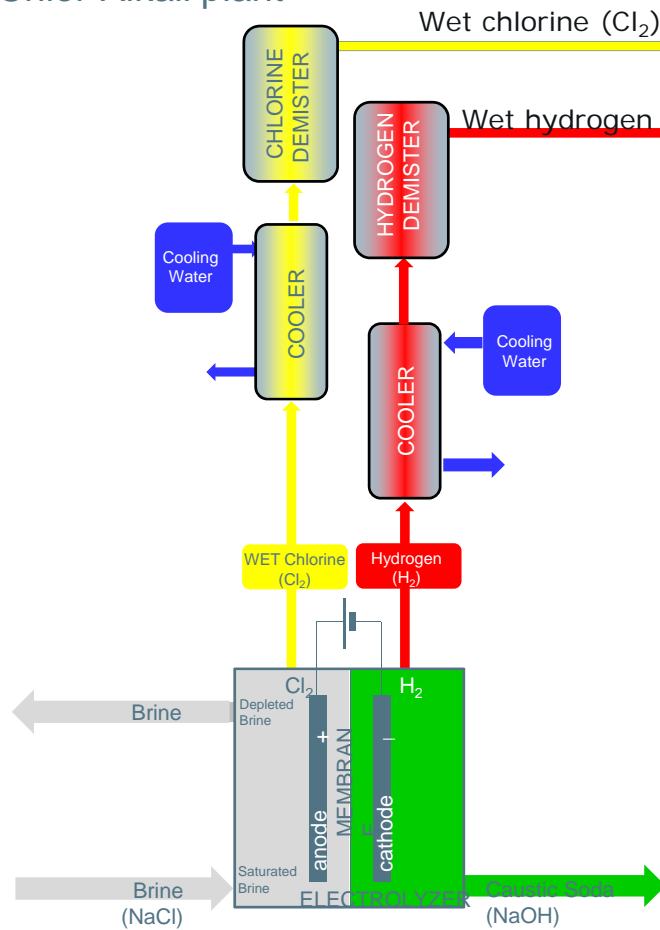
$$\epsilon = 1 - (0.351 + 0.256\beta^4 + 0.93\beta^8) \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{1}{k}} \right]$$

$$P_2/P_1 = \text{Throat pressure to inlet pressure ratio (dimensionless)} \\ = (P_{F \text{ PIT-2801-40}} - 0.03606 * H_{W \text{ FIT-2801-52A}}) / P_{F \text{ PIT-2801-40}}$$

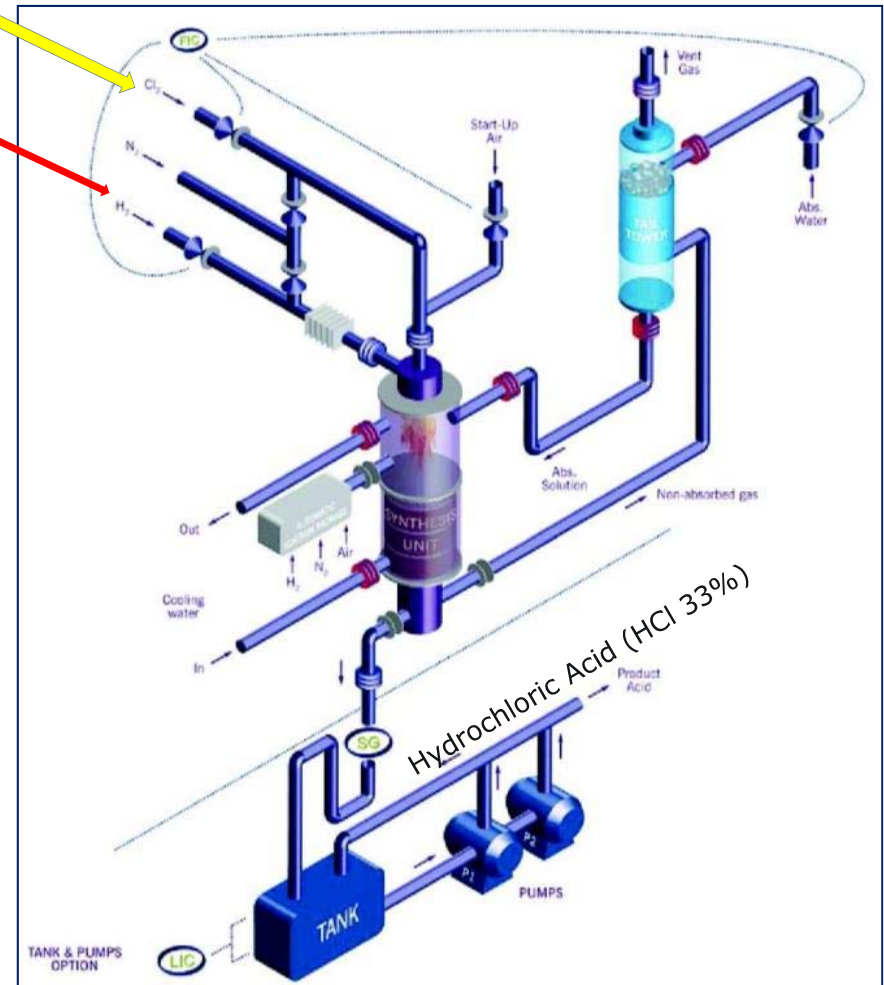
Enhanced safety for HCL synthesis units

MERSEN – process control & selection of control elements

Typical Chlor-Alkali plant



MERSEN Sintaclor package



If the compositions change and are not detected and corrected in the meter and control algorithms, explosions can occur.

Enhanced safety for HCL synthesis units

MERSEN – process control & selection of control elements

AppliTek



MERSEN “partners” with AppliTek to offer their expertise with on-line analyzers

- Hydrogen (H₂) and Chlorine (Cl₂) analyzers

On-Line measurement of oxygen (O₂) content in chlorine (Cl₂) feed – especially important for “sniff” or “weak” gas
→ Also an indication of the membrane quality / lifetime
→ Must adjust hydrogen consumption (H₂+Cl₂ → 2HCl and 2H₂+O₂→ 2H₂O) to avoid excess of chlorine OR over-consumption of hydrogen

On-Line measurement of oxygen (O₂) content in hydrogen (H₂) feed to keep the gas within the flammable limits to avoid a possible explosion
- Measurement of other inerts in H₂



Sabic Innovative Plastics
BoZ The Netherlands
Add-on to H₂ in WET Cl₂



Westlake Vinyl Company LP
Geismar LA USA
New chlorine plant project

If the compositions change and are not detected and corrected in the meter and control algorithms, explosions can occur.

Enhanced safety for HCL synthesis units

MERSEN – process control & selection of control elements



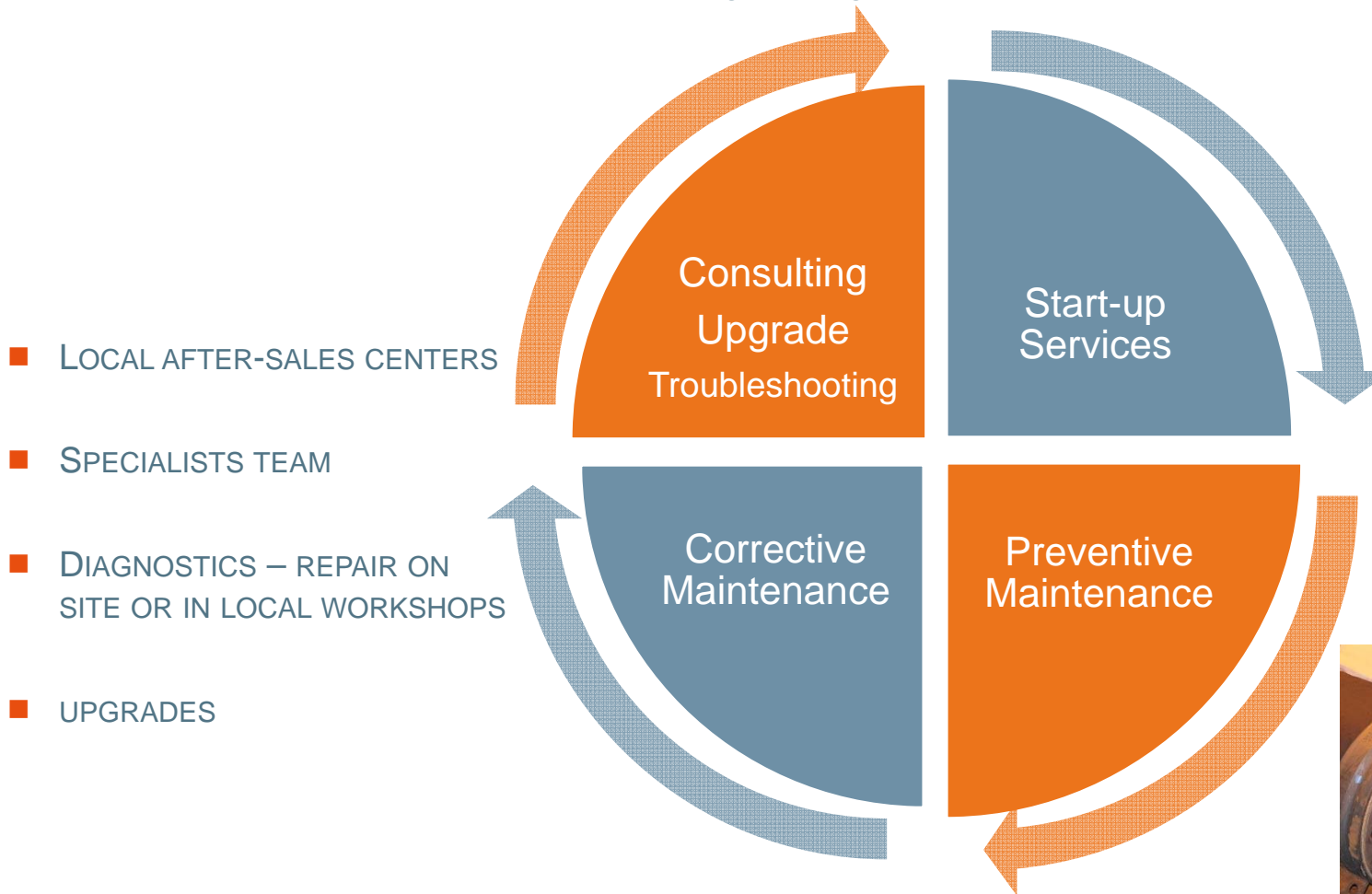
- **If flow meters and their algorithms are not correctly engineered and calibrated, flow calculations will be in error**
 - Very dangerous when trying to operating with low excess H₂
 - An upset condition can be disastrous and lead to the crossing of the stoichiometric boundary and an explosion can occur
 - Most older installations (prior to installation in ~2005) have major meter issues and control issues that have or can lead to “incidents”
 - These need to be corrected
 - Additionally, where “wet” feed gases are being used directly from the electrolytic cells, flow meter algorithms and controller algorithms need to compensate for changing saturated conditions (V%H₂O in gas stream) and or changing compositions as a result of membrane ageing or process upsets
 - most important for the H₂ stream
 - Since the MW (molecular weight) of H₂ is so low, any change in V% of H₂O in this stream will greatly affect the MW and then affect the meter reading and the H₂ controller set point algorithm
 - This is also an “accident” waiting to happen

If the compositions change and are not detected and corrected in the meter and control algorithms, explosions can occur.

Enhanced safety for HCL synthesis units

MERSEN – process control & selection of control elements

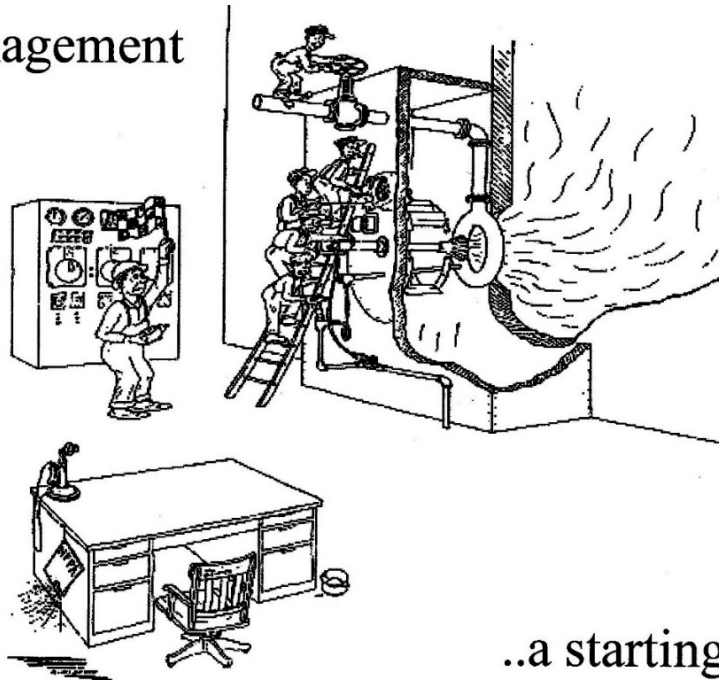
- MERSEN offers its “audit” and engineering services to find and correct these errors



Enhanced safety for HCl synthesis units

MERSEN's BMS – Burner Management System

Burner Management Systems..



..a starting point.

- Before 1990, almost all HCl synthesis systems started under vacuum “manually” and “blind”
- Most “incidents” (burner pops or explosions) historically have happened and are still happening during the “light up” (start up)
- It is about time that we move out of the “dark ages” and establish a safe & scientific start up system

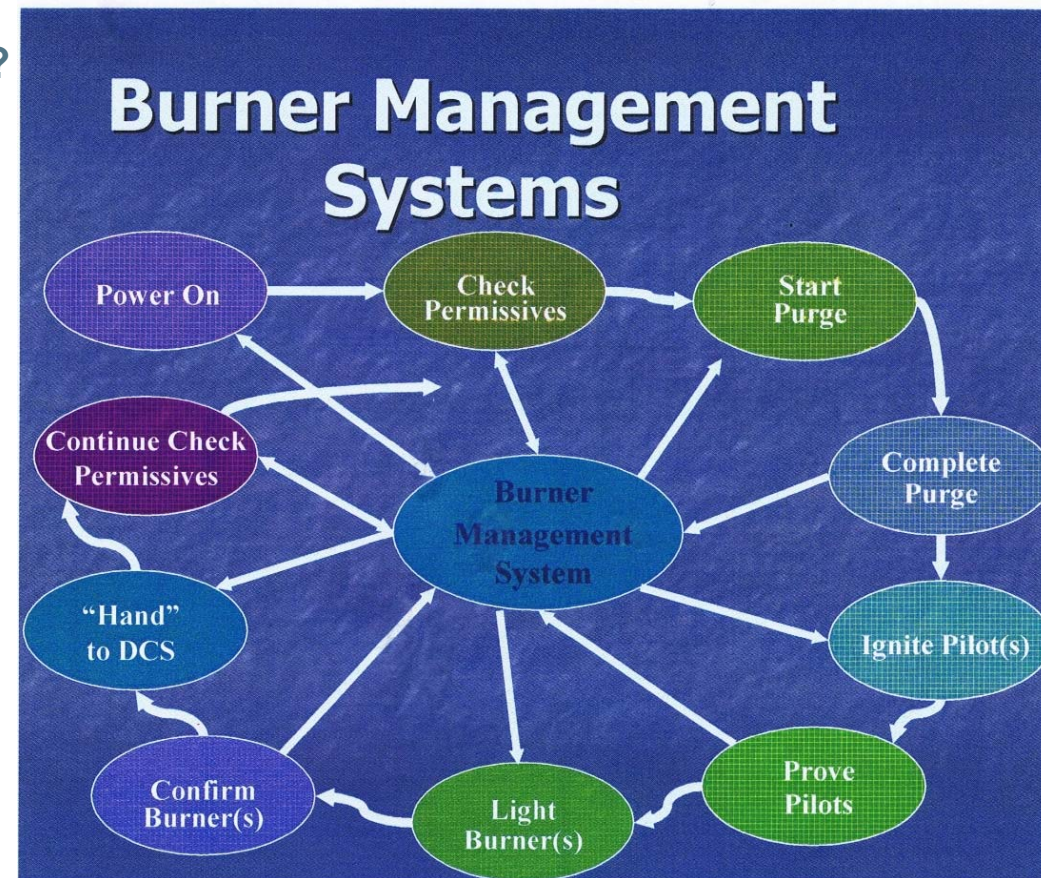
Enhanced safety for HCL synthesis units

MERSEN's BMS - a major safety development



Burner Management System – What does it do?

- Safely purges the system with nitrogen at start up & shut-down of burner
- Sequence burner ignition through safe start-up
- Supervise safety limits during operation
- Supervise the flame presence during operation
- Sequence a safe shutdown at end of cycle
- Integrate with the process control system for proper fuel (H₂) and oxidizer (Cl₂ and/or air) flows



Enhanced safety for HCL synthesis units

MERSEN's BMS-integrate to the DCS



Controller (DCS) :

Set point, Start/Stop mode, programming, auto-mode, capacity increase, change process variables.

...

(In the Process Industry, Controller is often a **DCS** = **D**istributed **C**ontrol **S**ystem or a **PLC**= Programmable Logic Controller in a control room)



Burner Management System :

MERSEN BMS can be located at the unit or in a clean area or control room

- Typically it integrates (handshakes) to the control system (DCS) via DCS programming

Enhanced safety for HCL synthesis units

MERSEN's BMS



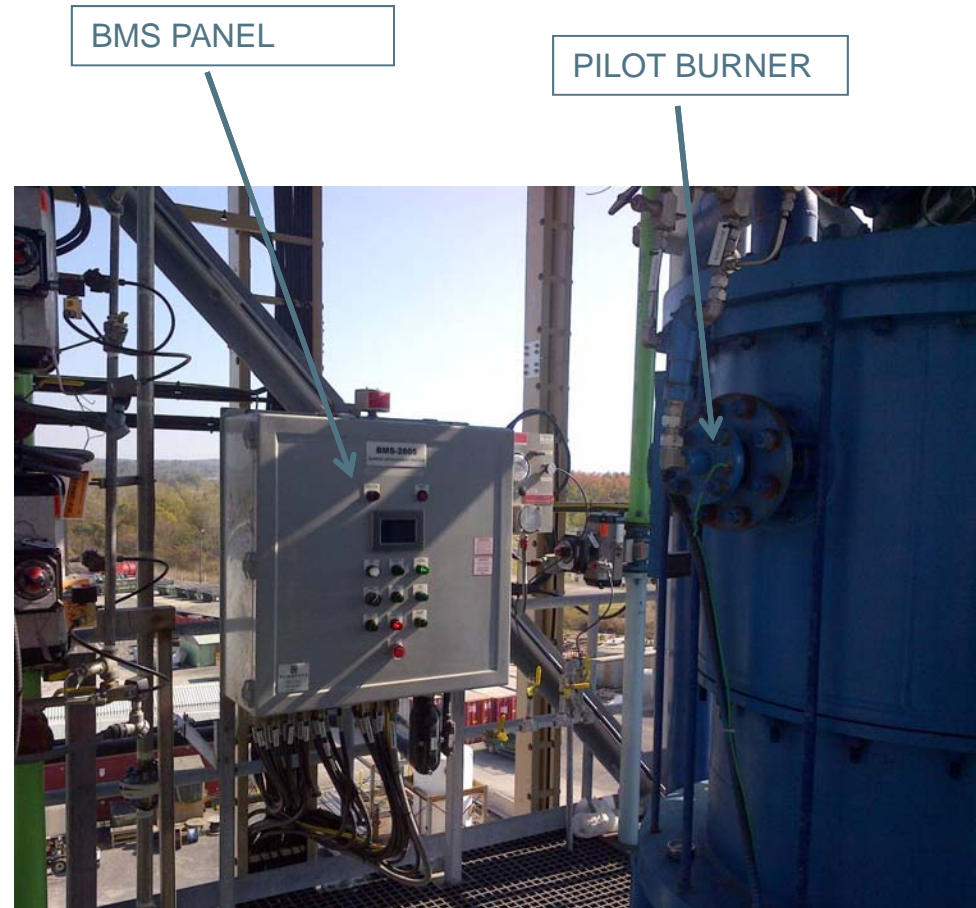
Burner Management System – other objectives

- BMS should be separate from any other control system and must be fail safe
- NFPA86 & EN-743 have strict guidelines on what can be used as the safety devices within a BMS



- For NFPA , flame detectors, temperature interlocks & safety shut-off valves shall be “listed” for combustion safety service or “approved” if a listed device is not available
 - “listed” means it has been tested and certified as safe for use by a Listing agency (like UL, CSA, FM, CE, etc.)
 - “approved” means device has been evaluated by the owner or an outside authority (like an insurance underwriter) and is “approved for service” but does not necessarily carry a stamp or listing

- MERSEN takes the approach to use “listed” devices wherever possible to avoid further headaches (“approval process”) for the owner



Enhanced safety for HCL synthesis units

MERSEN's BMS-Combustion Safeguard

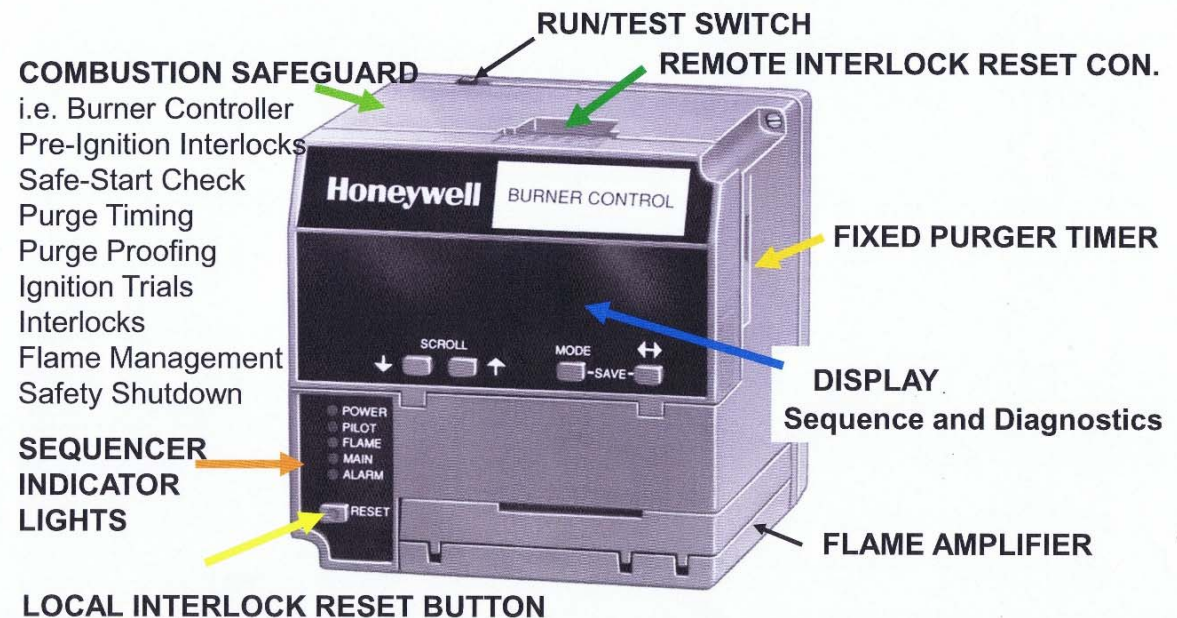


Burner Management System – Combustion Safeguard

- The combustion safeguard (logic solver) is the key safety “brains” for the system
- It can either be a “listed” device or a PLC (programmable logic controller) that meets additional requirements as set forth in NFPA86 section 8.4
 - **MERSEN uses a “listed” Honeywell combustion safeguard microprocessor based system**
- PLC's if used need to be third party certified to IEC 61508 and have a minimum SIL2 rating
- many other stipulations are required for PLC's or safety PLC's
- this can put very onerous responsibilities on the owner & will be much more expensive

Honeywell

Combustion Safeguard - Anatomy of a Burner Controller



- The Honeywell system is well suited to a single burner system such as that used in a MERSEN HCL synthesis unit system's BMS package

Enhanced safety for HCL synthesis units

MERSEN's BMS-Interlocks

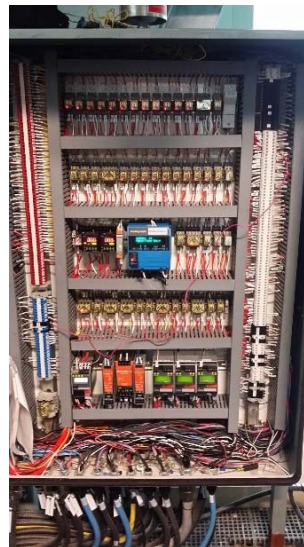


Burner Management System – interlocks

- The combustion safeguard (logic solver) is the key safety “brains” for the system but is not the entire system
 - many other components make up the package including many safety devices and interlocks in the field that mate to the logic solver to form a fail safe package
 - includes pressure switches, flow switches, valve position limit switches, etc. which are hardwired into the BMS control panel package
 - The BMS panel design integrates all of these interlocks with the logic solver



BMS PANEL INTERIOR



BMS PANEL EXTERIOR

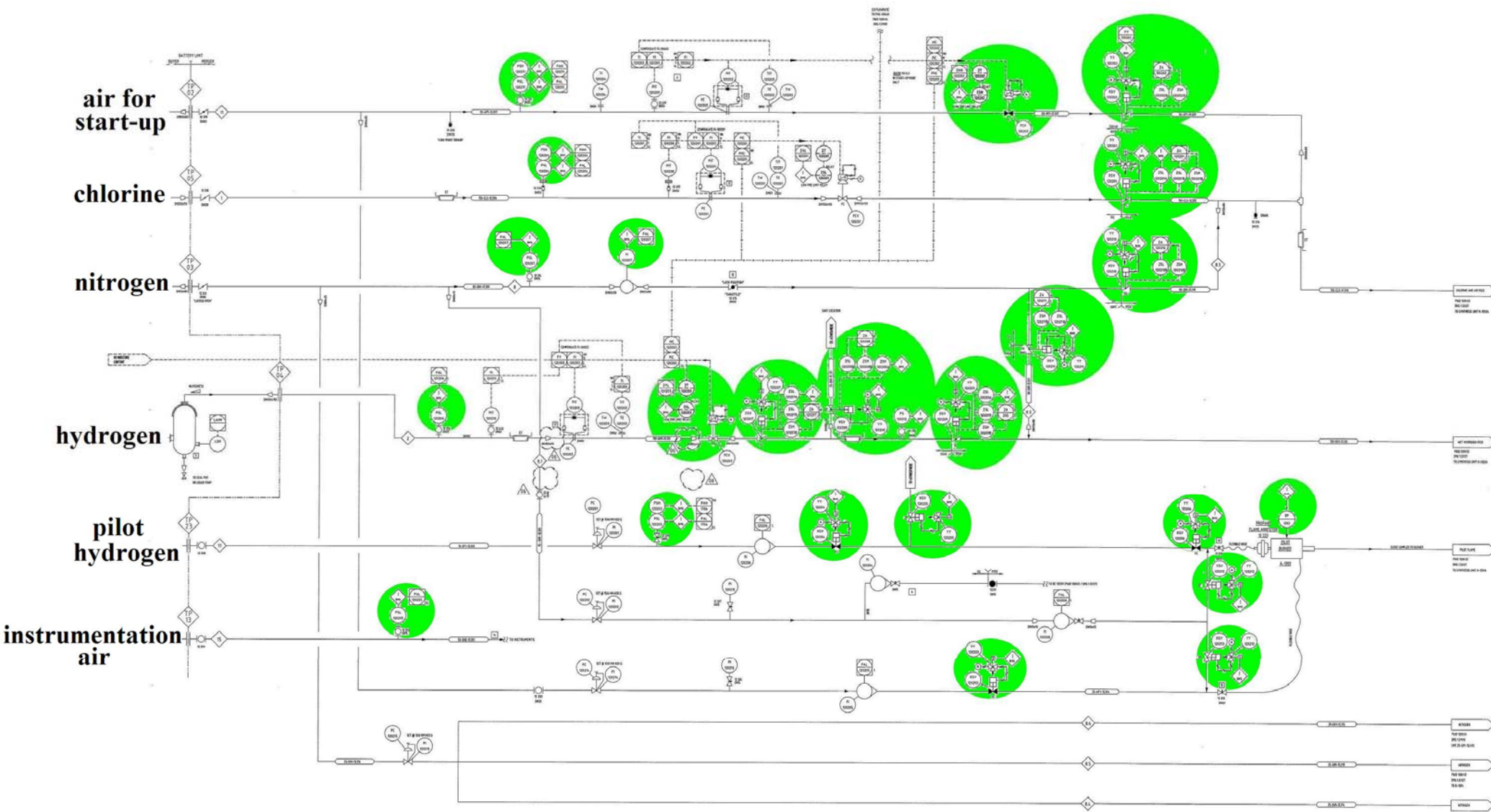


AUTO-IGNITER INSTRUMENT PACKAGE



Enhanced safety for HCL synthesis units

MERSEN's BMS- additional safety devices required for a safe system



Enhanced safety for HCL synthesis units

MERSEN's BMS- recent references in the world

■ EUROPE : (5)

- France : 3
- Germany : 2

■ AMERICA : (15)

- Argentina : 1
- Canada : 4
- Peru : 2
- USA : 10

■ ASIA / OCEANA: (5)

- Indonesia : 3
- Korea : 1 ; New Zealand: 1

■ MIDDLE-EAST : (5)

- Kuwait : 1
- Qatar : 2
- UAE : 2

BMS packages linked with
fully automatic start-up.
Customized automation for each project.



■ SAFETY :

Exclusivity : Mersen's Burner Management System (BMS) is the only safety protection according to EN 746-42 "industrial thermo-processing equipment / Safety requirements for combustion and fuel handling systems" and/or NFPA 86.

Mersen's BMS can be TÜV, CSA or other approval agency certified.

Enhanced safety for HCL synthesis units

CONCLUSION



- **SAFETY SHOULD NEVER BE AN OPTION**
 - BMS is like ABS® brakes or passenger AIRBAGS® when you purchase a car !
 - A BMS protects your assets
- **MERSEN IS THE ONLY ONE TO HAVE STUDIED, ENGINEERED, DEVELOPED AND SUPPLIED BMS PACKAGES FOR HCL BURNERS**
- **MERSEN IS THE LEADER DEDICATED TO CONTINUOUS SAFETY & OPERATIONAL IMPROVEMENT**

MERSEN safety enhancements

- **Material selection**
- **Safe equipment design**
- **Control philosophy and Safe practices**
- **Process control & selection of control elements**
- **BMS- Burner Management System**



**If you need an HCl production unit, you
need to discuss the safe choices offered**

by



THANK YOU FOR YOUR ATTENTION



November 2016 – Buenos Aires

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