SGL Group`s outstanding expertise – HCl synthesis units with steam generation

CLOROSUR BUENOS AIRES, ARGENTINA

NOV 2016
## HCl syntheses with steam generation at a glance

<table>
<thead>
<tr>
<th>Criteria</th>
<th>SGL offerings</th>
<th>Customer`s benefit (USPs)</th>
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</thead>
</table>
| Product variety           | HCl acid synthesis / HCl gas synthesis  
Dry feed gases / wet feed gases/ oxygen rich feed gases / ...  
Operation at ambient conditions or under pressure / ... | SGL offers a broad variety based on individual customer requirements.  
**Broad base. Best solutions.** |
| Capacity                  | Up to 160 t/d based on 100% HCl                                            | Large operating range from 25% to 100% of nameplate capacity                             |
| Product quality           | Chlorine free  
Iron contamination < 1 mg/l HCl possible                                  | Pure HCl acid                                                                           |
| Energy efficiency         | Steam generation up to 10 barg                                               | Short payback times due to energy savings                                                |
| Project execution / Lead time | Fully backward integrated - from own material production to skid mounted units | One stop shop – no additional interfaces, i.e. shortest lead times possible              |
| Services                  | SGL concept includes the full life cycle management (from feasibility study to commissioning, after sales service and maintenance) | Fast, flexible and professional global support by SGL experts – also on customer`s site |
Agenda

Process description

HCl steam syntheses technology by SGL
- Ecosyn technology
- Membrane wall technology

SGL`s competences at a glance

Summary
HCl synthesis – a rough process description

• Strong exothermic reaction of hydrogen and chlorine gas to HCl gas (flame temperature: > 2.000 °C / 3.630 °F)

• Combustion chamber out of coated carbon steel

• Graphite parts of the HCl synthesis are incorporated in a cooling water leading steel shell

• For HCl acid synthesis units:
  – Absorption of HCl gas in a falling film absorber
  – Absorption media is either water or diluted hydrochloric acid
  – Residual gas (containing inert gas and hydrogen) is cleaned in a vent scrubber
Agenda

Process description

HCl steam syntheses technology by SGL

- Ecosyn technology
- Membrane wall technology

SGL`s competences at a glance

Summary
Abstract of our HCl synthesis units portfolio

- Internal scrubber
- Counter-current series
- Co-current series
- Top fired series
- External scrubber
- External scrubber
- External scrubber
- Membrane Wall series
- External absorber & scrubber

HCl syntheses with steam generation
Bottom burner is technology of choice ...

...as it stands for:

+ low hydrogen excess required due to high residence time, i.e. **low operation cost**
+ **highest availability** due to fast and easy exchange of the burner tubes from ground level
+ low downtimes due to unique flushing system which allows for **cleaning** of burner tubes with water **during operation**
+ **highest safety** standard due to rupture disk located in a safe surrounding on top of the unit and fully automated ignition system
+ **easy access** to instruments, sight glass and burner **at ground level** – no stairways need to be used
+ **dry combustion** chamber allows complete reaction of free chlorine
+ **free Cl$_2$** in product $< 1$ ppm (depending on feed gas composition) leads to a crystal clear acid
+ high **HCl acid concentration up to 37 %** possible
+ product outlet nozzle is elevated – **no pumps** required
HCl syntheses with steam generation by SGL

**ECOSYN® synthesis**
- Economic design for capacities < 60 t/d HCl
- Gas cooling in synthesis down to 300°C
- Absorption of HCl-gas in external shell & tube heat exchanger
- Steam production approx. 60 % higher and cooling water requirement approx. 30 % lower compared to membrane wall synthesis
- Shortest payback times

**Membrane wall synthesis**
- Economic design for capacities > 60 t/d HCl
- Gas cooling in synthesis down to approx. 1000°C
- Absorption of HCl-gas in internal absorption section/block elements
Agenda

Process description
HCl steam syntheses technology by SGL

- Ecosyn technology
- Membrane wall technology

SGL`s competences at a glance

Summary
Key advantages – example ECOSYN®

- Standard DIABON® burner design
- Absorption of HCl-gas in standard DIABON® shell & tube heat exchanger
- Steam pressure up to 10 barg
- Capacity up to 60 t/d (100 % HCl basis)
- Broad range of operation from 25 % to 100 % of nameplate capacity
- Shortest payback times due to additional steam generation
Agenda

Process description
HCl steam syntheses technology by SGL
- Ecosyn technology
- Membrane wall technology

SGL`s competences at a glance

Summary
Key advantages – Membrane wall technology

- Standard DIABON® burner design
- Absorption of HCl-gas with DIABON® falling film absorber technology
- Steam pressure up to 10 barg
- Capacity up to 160 t/d (100 % HCl basis)
- Broad range of operation from 25 % to 100 % of nameplate capacity
- Shortest payback times due to additional steam generation
Agenda

Process description
HCl steam syntheses technology by SGL
- Ecosyn technology
- Membrane wall technology

SGL`s competences at a glance

Summary
We execute according to specific local regulations

**Customer & Task**
- International customers ask for technical solutions which are in accordance with local regulations

**Benefit for customer**
- No additional interfaces or inspection of components by third parties required
- Shortest possible project execution time

**Competence / SGL solution**
- Certified to handle orders according to international regulations and documentation requirements, e.g. AD2000, ASME (U-stamp), ANSI, DIN, GB 150, GOST, JIS, KOSHA, ...
State-of-the-art simulation tools enable lowest operating cost at highest performance

**Competence / SGL solution**

- Inhouse simulation competences, e.g. optimization of temperature profiles by Ansys/FEM calculation
- Expertise in process design and engineering

**Benefit for customer**

- Tailor-made design ensures maximum heat recovery and minimum operating cost
- Improved total product lifetime due to optimal thermal design of the total unit
- Prolonged maintenance intervals
Our engineering competences enable you to get ahead your competitors

**Competence / SGL solution**

- More than 60 inhouse engineers comprising all disciplines; e.g. CAD, process design
- Shortest lead times due to less interfaces
- Inhouse 3D layout design competence

**Benefit for customer**

- Only one contact person
- Highly efficient planning process; tailor-made adjustments possible based on direct customer feedback during engineering and design phase
- Fast commissioning – no “on-site” re-work
Fully skid mounted units for utmost efficiency

- Modular construction possible
- Lower costs than field construction
- Construction proceeds offsite, no waiting for permits
- Shorter project schedules
- Minimized engineering expenditure
- Single-source responsibility for entire process
- Reduced safety risk
- Minimal plant site interruption
- Lump sum pricing
Agenda

Process description
HCl steam syntheses technology by SGL
- Ecosyn technology
- Membrane wall technology
SGL`s competences at a glance

Summary
We offer a broad scope of supply – it's your choice!

<table>
<thead>
<tr>
<th>Equipment</th>
<th>• Synthesis unit including burner, combustion chamber, absorber and scrubber plus heat recovery option</th>
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</table>
| I&C       | • Field instrumentation for automatic start up  
            • Field instrumentation for control  
            • Field instrumentation for safety interlocks  
            • Control panel incl. safety system  
            • Local ignition panel |
| Fittings, Piping, Steel | • Flame arrestors, manual valves, PTFE bellows  
                            • Piping: Steel PTFE, PP, FRP, CS  
                            • Steel structure and skid mounting |
| Engineering & Execution | • Feasibility study, Basic and Detail Engineering  
                            • Commissioning including on-site training and final documentation |
DIABON® Porous Reactor

-An introduction-

-CLOROSUR BUENOS AIRES, ARGENTINA

NOV 2016
Agenda

Applications

Process description
Scientific & chemical background
Product description
Summary
DIABON Porous Reactor technology offers a broad range of applications

- **Destruction of hydrochlorofluorocarbons (HCFCs)**
  - E.g., destruction of refrigerants (e.g. R12, R22, R134a etc.)

- **Off-gas treatment**
  - E.g., waste gas stream containing organics and HCl

- **Synthesis of hydrogen chloride (HCl)**
  - E.g., synthesis of HCl by reaction of Cl\textsubscript{2} with CH\textsubscript{4}

- **Oxydizing or reducing regime**
  - E.g., for production of chlorine free HCl acid

- ...
Agenda

Applications
Process description
Scientific & chemical background
Product description
Summary
A rough process description

- Feed gas enters the porous reactor together with air and natural gas (hydrogen source)

- Thermally induced reaction takes place in a porous structure instead of an open flame

- Acids (e.g. HF, HCl) can be concentrated in a falling film absorber

- Off-gas is treated in an external caustic soda scrubber
PFD of a typical porous reactor process
Agenda

Applications
Process description
**Scientific & chemical background**
Product description
Summary
Porous reactor – design limitations

- Solids not allowed due to fouling
- Liquids to be evaporized before entering the reaction section
- In case of direct cooling by steam, super-heated steam (~ 180 °C) is required in order to avoid condensation
- Water saturation of feed and fuel not critical, but to be respected (impact on reactor dimension)
Porous reactor technology meets tight environmental regulations

- No formation of dioxin and furan due to sudden quenching below 200 °C (avoidance of de novo synthesis)
  - Dry quenching in graphite block heat exchangers
  - Dioxin / furan < 0,1 ng/Nm³

- Formation of thermally induced NOx ("Zeldovich mechanism") is limited due to
  - Low temperatures < 1.500 °C (typical temperature around 1.300 °C)
  - Low dwell time < 2s

- No CO formation in oxidizing regime

- Emissions below limitations of TA-Luft
  - E.g., HCFCs < 20 mg/Nm³, HCl < 30mg/Nm³, Cl₂ < 3 mg/Nm³, NOₓ < 100mg/Nm³
Agenda

Applications
Process description
Scientific & chemical background
Product description
Summary
DIABON® Porous reactor – in a nutshell

- Start-up and shut down times below 15 minutes – no standby mode required
- Process temperature up to 1,500 °C (typical operating temperature between 1,250 °C and 1,400 °C)
- Thermal power up to 2,500 kW
- Porous reactor is an approved technology for the destruction of CFC, HCFC, carbon tetrachloride and methyl chloroform(*)
- No formation of NO\textsubscript{x} and / or dioxin due to low dwell time, optimal heat transfer and sudden quenching

Agenda

Applications
Process description
Scientific & chemical background
Product description
Summary
SGL Group`s DIABON® porous reactor is unique

**USPs of SGL Group’s technology**

- **Need-based operations** enabled by extremely short start-up and shut off times (ca. 15 minutes)
- **Energy efficient** as no standby mode is required and wide control range from 10% to 100%
- **High equipment availability and long lifetime** due to highest corrosion resistance
- **High safety** due to **low reaction volume** based on an optimal heat transfer and **extreme short emergency shut off time** of 2 s
- Up to 60% **less space requirement** compared to a conventional combustion chamber
- **Complete destruction of critical substances** and optionally **recovery of acids** (e.g. HCl, HF)

**Standard applications**

- Destruction of HCFC, e.g. recycling of refrigerants
- Waste gas / off-gas treatment in chemical plants
- HCl synthesis, e.g. with methane and chlorine
Thank you for your attention!
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Benefits of Steam Generation with HCl Synthesis

1000 tpd HCl 100%
with Steam Recovery
Benefits of Steam Generation with HCl Synthesis

- Steam is an important consumable in the Chlor-Alkali Process, necessary to maintain the required process temperature conditions and also mainly to concentrate caustic from 32% up to 50% NaOH.

- Steam consumption is generally in the range of 550 - 800 kg Steam per t NaOH produced contributing to increase the Operating Cost by about $15 – 30 / t NaOH.

- Steam Generation in Chlor-Alkali Plants is normally fueled with Natural Gas and excess Hydrogen not consumed in the HCl Synthesis.

- Some chlor-alkali projects require only 50% NaOH and 32-35% HCl, and sodium hypochlorite is a not desired product, and thereby H2 is not further available for steam generation.
Benefits of Steam Generation with HCl Synthesis

40 - 60% Energy Recovery in the HCl Synthesis Furnace equivalent to 500 - 650 kg Steam Generation per ton HCl 100%

HEAT GENERATION AT HCl SYNTHESIS

HCl (g) + H2O
84 m³/(h x t HCl)

CW

H2+Cl2= 2HCl

STEAM <10 barg
500-650 kg/tHCl

COMBUSTION HEAT
700 kW/ton HCl

2000 grd C

Boiler Feed Water
Benefits of Steam Generation with HCl Synthesis

The following case shows the operating conditions in which the steam generation cost is virtually zero, in which part of the H2 produced fuels the steam boiler in order generate the necessary steam to concentrate the caustic production from 32% up to 50% NaOH.

The calculation is based on following assumptions:

- **H2 / Cl2 ratio in the HCl Synthesis** < 1.10
- **LHV of H2** 120 MJ / Kg H2
- **H fg, Latent Heat of Evaporation** 2,30 MJ / Kg Steam at 5 bar g
- **Boiler Efficiency** 85%
Benefits of Steam Generation with HCl Synthesis

Steam Generation Alternatives

STEAM GENERATION COST: $ 0 / t NaOH

Main Products Required

- SODIUM HYPOCHLORITE LIQUID Cl2
  - 4.07 t Cl2 / h

- CAUSTIC SODA
  - 50% NaOH
  - 9 t NaOH 100% / h

- HYDROCHLORIC ACID
  - 32-35% HCl
  - 4.93 t HCl 100% / h

**ELECTROLYZER**
- 10 t NaOH / h
- E = 21 MW

**NaOH**
- 10 t/h
- 9 t/h

**NaOH CONCENTRATION**
- 32% -- 50%
- 0.50 t STEAM / NaOH 100%

**5 bar g STEAM**
- 4.5 t/h

**SODIUM HYPOCHLORITE LIQUID Cl2**
- Cl2 4.07 t/h
- Cl2 4.80 t/h

**Mol Ratio H2/Cl2**
- 1.10

**HCl SYNTHESIS**
- 4.93 t HCl / h
- Without Steam Generation

**STEAM BOILER UNIT**
- 4.5 t NaOH / h

**STEAM CONSUMERS PROCESS HEATING**

**H2 Vent**
- 0.06 t/h

**NAT GAS**
- t/h
Benefits of Steam Generation with HCl Synthesis

In some cases the main product required by the market is mainly caustic soda and hydrochloric acid and only a minimum amount of Liquid Cl2 or Hypochlorite is required.

The maximum amount of Cl2 which can be converted into HCl is given by the fact that we need to operate the HCl Unit with 5 - 10% more H2 than Cl2 (as moles)

The balance of about 10% of the Cl2 not consumed in the HCl Unit must be converted either into Sodium Hypochlorite or to Liquid Cl2.

In this case all necessary steam to concentrate about 90% of the caustic produced from 32% to 50% NaOH can be generated by the HCl Synthesis Unit.
Benefits of Steam Generation with HCl Synthesis

Steam Generation Alternatives

STEAM GENERATION COST: $ 0 / t NaOH

ELECTROLYZER
10 t NaOH / h
E = 21 MW

NaOH
10 t/h

NaOH
1 t/h

NaOH
9 t/h

NaOH CONCENTRATION
32% → 50%
0.50 t STEAM / NaOH 100%

5 bar g STEAM
4.5 t/h

< 10 bar g STEAM
5.3 t/h

STEAM CONSUMERS
PROCESS HEATING

STEAM BOILER UNIT
4.5 t NaOH / h

SODIUM HYPOCHLORITE
LIQUID Cl2

Cl2
0.86 t/h

Cl2
8.0 t/h

Mol Ratio H2/Cl2
1.10

H2 SYNTHESIS
8.2 t HCl / h
0.65 t Steam / t HCl 100%

H2
0.25 t/h

H2
0 t/h

H2 Vent
0.06 t/h

SODIUM HYPOCHLORITE LIQUID Cl2
0.86 t Cl2 / h

CAUSTIC SODA
50% NaOH
9 t NaOH 100% / h

HYDROCHLORIC ACID
32-35% HCl
8.2 t HCl 100% / h

NAT GAS
t/h
Benefits of Steam Generation with HCl Synthesis

In other cases no Liquid Cl2 or Hypochlorite is desired, and the only product output of the plant shall be 50% NaOH and 35% HCl.

The excess of H2 needed for the HCl Synthesis unit can be provided by a H2 generator by water electrolysis.

Also in this case all necessary steam to concentrate about 100% of the caustic produced from 32% to 50% NaOH can be generated by the HCl Synthesis Unit.
Benefits of Steam Generation with HCl Synthesis

Stein Generation Alternatives

STEAM GENERATION COST: $0 / t NaOH

Main Products Required

- O2
  - 0.40 t/h

- H2 GENERATOR
  - 0.025 t H2 / h
  - E = 1.6 MW

- ELECTROLYZER
  - 10 t NaOH / h
  - E = 21 MW

- NaOH
  - 10 t/h

- NaOH
  - 0 t/h

- SODIUM HYPOCHLORITE LIQUID CL2
  - NaOH CONCENTRATION
    - 32% --> 50%
    - 0.50 t STEAM / NaOH 100%

- Cl2
  - 8.86 t/h

- Cl2
  - 0 t/h

- H2
  - 0.275 t/h

- H2
  - 0 t/h

- H2 Vent
  - 0.06 t/h

- NaOH CONCENTRATION
  - 32% --> 50%
  - 0.50 t STEAM / NaOH 100%

- Mol Ratio H2/Cl2
  - 1.10

- HCl SYNTHESIS
  - 9.1 t HCl / h
  - 0.65 t Steam / t HCl 100%

- < 10 bar g STEAM
  - 5.9 t/h

- 5 bar g STEAM
  - 5.0 t/h

- STEAM CONSUMERS
  - PROCESS HEATING

- STEAM BOILER UNIT
  - 5 t NaOH / h

- NAT GAS
  - t/h

- SODIUM HYPOCHLORITE LIQUID Cl2
  - 0 t Cl2 / h

- CAUSTIC SODA
  - 50% NaOH
  - 10 t NaOH 100% / h

- HYDROCHLORIC ACID
  - 32-35% HCl
  - 9.1 t HCl 100% / h
Benefits of Steam Generation with HCl Synthesis

Conclusions

- Based on a production capacity of 10 t/h NaOH,
- Energy cost $10 /MBTU,
- Steam cost $30 / t,
- Steam consumption 5 t/h to concentrate 32% up to 50% NaOH

We can achieve through steam generation in HCl Synthesis

Annual Cost Savings of $1.3 MM