Use of carbon fiber reinforced DIABON® graphite tubes in shell and tubes phosphoric acid evaporators

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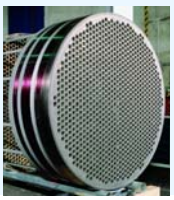
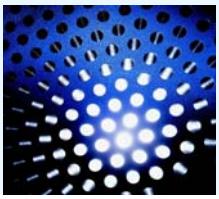
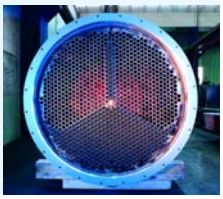

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Process Technology

Overview of Subjects

1. Process and Process Conditions
2. Use of Synthetic Resin Impregnated Graphite
3. Historical use of Graphite Block Heat Exchangers
4. Use of Graphite Shell and Tubes Heat Exchangers
5. Diabon tubes
6. State of the Art Construction
7. Design Options
8. Operational recommendations
9. Graphite versus nickel alloys
10. Conclusions

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1. Process and Process Conditions

- Different processes
- Concentration processes
- State of the art design
- Fouling

➔ Depending on the process, 1 to 3 evaporation stages

Different processes

- Different wet P_2O_5 processes out coming concentrations:
  - 28 to 30 % P_2O_5 for the conventional dihydrates (DH)
  - 30 to 32 % P_2O_5 for the hemihydrates recrystallization (HRC)
  - 32 to 36 % P_2O_5 P2O5 for the dihemihydrates (DHHH),
  - 40 to 42 % P_2O_5 for the hemihydrates (HH)
  - 40 to 54 % P_2O_5 for the hemidihydrates (HDH)
- P_2O_5 commercial grade is set at 54 %.

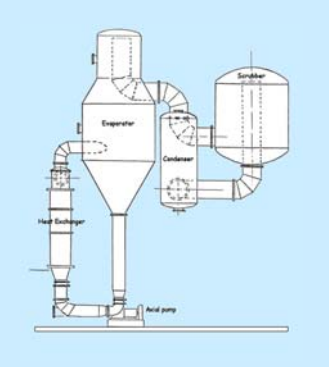
➔ Depending on the process, 1 to 3 evaporation stages

Many types of concentration processes used

- Originally, submerged combustion concentrators
  - Gas or fuel was burned directly in a pool a P_2O_5
  - Extremely polluting
- Natural circulation evaporators
  - Low efficiency
- Forced circulation evaporators
  - High efficiency

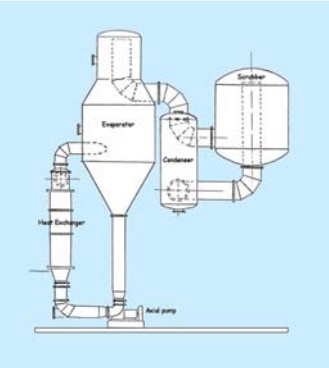
State of the art design

- Axial pump
  - Up to 12,000 m³/h (50,000 gal/min)
  - Usually in High alloys S28 or G30
- Heat exchanger
  - Up 1200 m²
  - Up to 1200 tubes
  - Up to 9m (30') long
- Up to 30 tons of steam per hour
  - by product of the sulfuric acid production
- Rubber lined piping and conical headers
  - Bromobutyls or chlorobutyls rubber



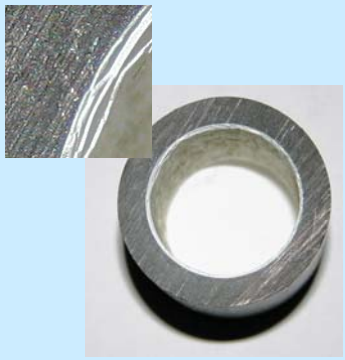
State of the art design

- Flash tank connected to vacuum group
  - Pressure 100 mbar (1,50 psi)
  - Acid boils between 80 and 90°C
- Single-effect evaporators
  - 800 kg (1760 lb) steam per ton of evaporation
  - 2,5 to 3 tons of LP steam per ton 54% P_2O_5 produced
- Multi stages evaporation units
  - 1St stage: 35 to 39 % P_2O_5
  - 2^{d} stage: 44 to 46 % P_2O_5
  - 3^{d} stage: 54 % P_2O_5
- Actual trend is to reduce the number of evaporation stage to reduce procurement costs.



Fouling is the key issue

- Scaling
  - Occurs because of concentration rise causes the sursaturation of gypsum
  - Deposit on the tube surface
  - Λ_{gypsum} = 0,73 W/m.K
  - Heat transfer coefficients
    - 1000 W/m².K when clean
    - 500 W/m².K when the unit is totally fouled up and requires cleaning



➔ Fouling cut the heat transfer efficiency by 2

2. Use of Synthetic Resin Impregnated Graphite

- Corrosiveness of green acid
- Graphite manufacturing process
- Carbon atoms rearrangement
- Impregnation
- Graphite properties

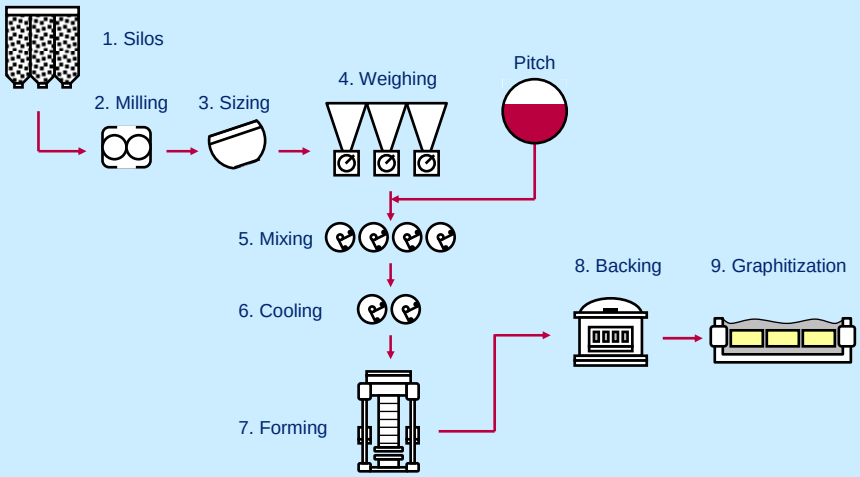
➔ Green acid is ultra corrosive

Corrosiveness of green acid

- P2O5 Pkas are 2.12, 7.21 and 12.67
  - Phosphoric acid is a very gentle acid when PURE !
  - Green acid contains all kinds of impurities
    - F-, Cl- contents depend mostly on the rock source
    - Green acid can be extremely corrosive
- Synthetic resin impregnated DIABON® graphite
  - Can handle the corrosiveness of any green phosphoric acid
  - Can be operated at high temperatures up to 200°C (392 F).

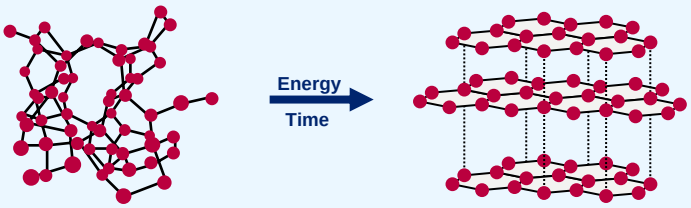
➔ Green acid is ultra corrosive

Manufacturing process overview



Carbon atoms rearrangement

- **Graphite crystal structure.**



Amorphous carbon

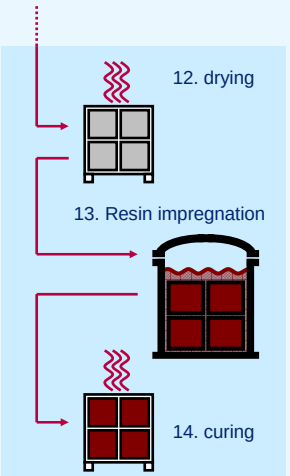
Graphite structure

High thermal conductivity
Easily machinable

➔ **Graphitization enhances material thermal conductivity.**

Synthetic resin impregnation

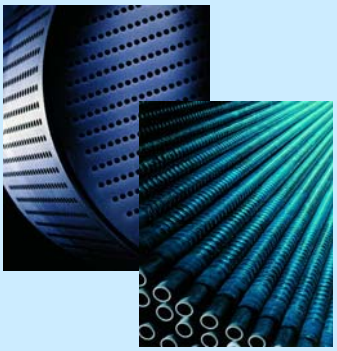
- Raw graphite components are heated to drive off the moisture.
- A specific proprietary resin is pushed under pressure into the graphite pores. The full impregnation is made in a single step.
- The graphite parts, containing the liquid resin, are cured in a furnace. The temperature is carefully ramped up to ensure a state of the art polymerization.



➔ **The result is a totally impervious Process Equipment graphite.**

Graphite properties

- The resulting composite material is fully corrosion resistant to most acids
  - Sulfuric acid, hydrochloric acid,
  - Industrial phosphoric acid
  - Very high thermal conductivity of
    - 80 W/m.K for tubes
    - 140 W/m.K for blocks
- Good mechanical strength in compression
- Fully impervious



3. Historical use of Graphite Block Heat Exchangers

- Graphite block heat exchangers
- Design
- Features

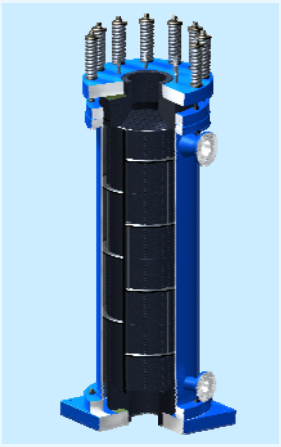
Graphite Block Heat Exchangers

- Cylindrical blocks are manufactured from monolithic cylindrical bars in several steps:
  - Machining to rough dimensions
  - Synthetic resin impregnation
  - Machining to final dimensions
  - Drilling on both sides
  - Finishing

➔ Process and service holes are free of resin

Block Heat Exchangers design

- A cylindrical blocks heat exchanger consists of:
  - A steel base plate
  - A bottom header
  - A stack of DIABON® blocks
  - A baffle cage
  - A top header
  - A steel shell
    - O'ring gasket
  - A top tightening plate
    - Tie rods
    - Springs to maintain the blocks under compression



Block heat exchangers features

- Modular design
- Block can be individually tested
- Simple maintenance

- Limited heat transfer efficiency with steam
- Sensitivity to thermal and mechanical shocks.
- In case of damaged block
  - whole unit shall be disassembled
  - cracked block must be replaced
  - whole unit shall be regasketed

  } 24 to 48 hours shutdown

- Larger unit means larger diameter blocks
  - More costly, block heat exchanger design is less competitive
  - Difficulty to extract condensates

4. Use of Graphite shell and tube heat exchangers

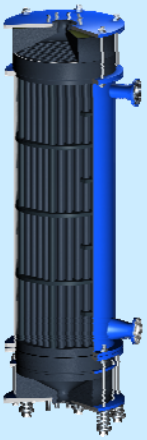
- Graphite shell and tube heat exchangers
- Design

Graphite Shell and Tubes Heat Exchangers

- As the size of phosphoric acid plants increased, came the need for larger and larger evaporators.
  - Graphite shell and tube heat exchangers
  - Three major issues in operation
    - Tubes cracking
      - Steam hammering, thermal stresses, fouling, tube erosion, sawing by sharp baffles, shearing stresses, aging, operational erosion
    - Splitting of tube sheets
      - Over-tightening, non-monolithic tube sheets, aging.
    - Erosion of the tube sheet
      - Too high process velocity

Design

- Shell and tubes heat exchangers are built of tubes mounted in cylindrical shells with the axis of the tubes parallel to that of the shell.



Design

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- The phosphoric acid to be concentrated flows within the tubes.

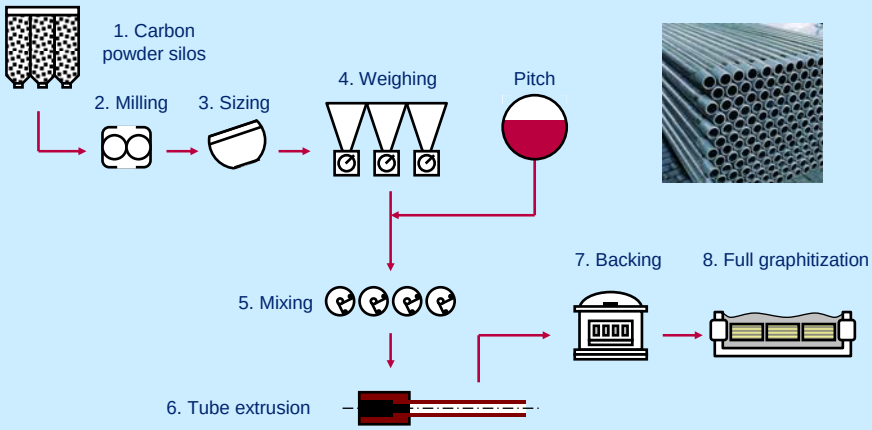
Design

- Shell and tubes heat exchangers are built of tubes mounted in cylindrical shells with the axis of the tubes parallel to that of the shell.
- The phosphoric acid to be concentrated flows through the tubes.
- The steam flows on the shell side. It flows from one baffle compartment to the next. The condensates come out at the bottom of the shell.

5. DIABON® tubes

- Tube manufacturing process
- Thermal conductivity
- Cemented joints
- Carbon fiber reinforced tubes
- Tubes sizes and pitch

DIABON® tubes manufacturing



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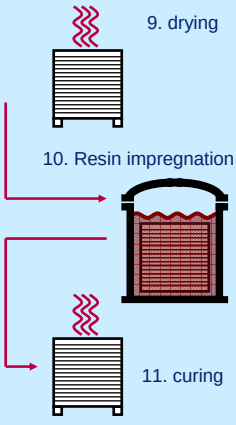
Synthetic resin impregnation

- **Raw graphite tubes are heated to drive off the moisture.**
- **A specific proprietary resin is pushed under pressure into the graphite pores. The full impregnation is made in a single step.**
- **The graphite tubes, containing the liquid resin, are cured in a furnace. The temperature is carefully ramped up to ensure a state of the art polymerization.**



➔ **The result is a totally impervious Process Equipment graphite.**

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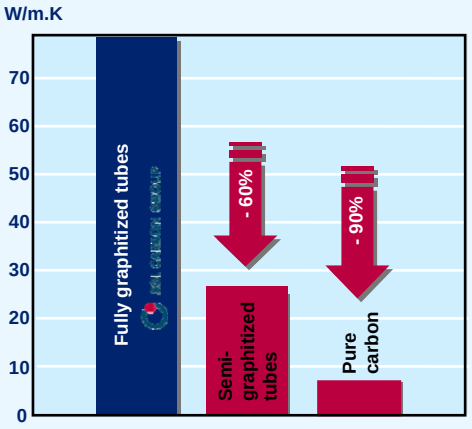
Process Technology

Tubes thermal conductivities as Comparison

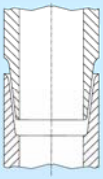
- SGL is committed to produce only fully graphitized tubes.
- Our tubes thermal conductivity is approximately 80 W/m.K.



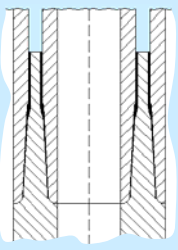
➔ SGL CARBON produces fully graphitized tubes

Cemented joints

- Tube / tube connection
  - 3m long single tubes are cemented
  - Maximum length 9,5m
  - Unique male / female connection profile



- Tube / tube sheet connection
  - Especially designed tube / tube sheet connection prevents shearing stresses



Carbon fiber reinforced tubes

- Fully graphitized and impregnated tubes are wrapped with pretensioned carbon fiber.
  - Significant mechanical reinforcement
  - Improved resistance to pressure surges
    - 250% better
  - Improved bursting pressure
    - 110 versus 80 bar at 20°C
    - 120 versus 75 bar at 50°C
  - Pressure holding even when cracked
    - Up to 3 bar differential pressure

Carbon fibber reinforced tubes

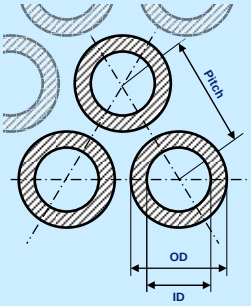
➔ SGL CARBON DIABON HF tubes bring a proven reliability to the process

Tube sizes and pitch

- 4 tubes types

Tube type	0	1	2	3
ID in mm	15	22	25	37
OD in mm	26	32	37	50
Pitch in mm	33	39	44	57

- Pitch = OD + 7 mm
- Triangular pitch at 60°



6. State of the art construction

- Baffles
- Tie rods
- Tubes
- Tube sheets
- Shell
- Headers
- Steel parts
- Expansion system
- Design data

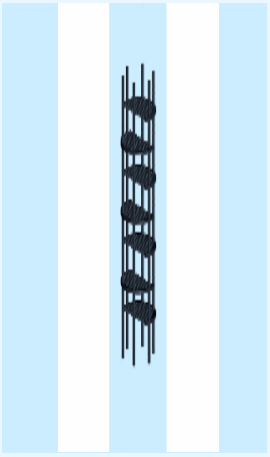
Baffles cage

- A shell and tubes heat exchanger consists in:
  - A baffles cage
    - Baffles in ®Diabon N
      - Same material as the tubes. No risk of cutting the tubes
    - Tie rods in ®Diabon NS
      - Same expansion as the tubes. No stress on the tube bundle or on the tube sheets.

➔ ®Diabon NS tie rods have the same expansion rate as the tubes.

Tubes

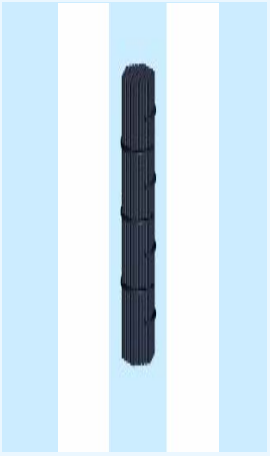
- A shell and tubes heat exchanger consists in:
  - A baffles cage
    - Baffles in ®Diabon N
    - Tie rods in ®Diabon NS
  - The ®Diabon NS1 or HF1 tubes



➔ ®Diabon NS or HF tubes are sturdy and have a very high thermal conductivity.

Tube bundle

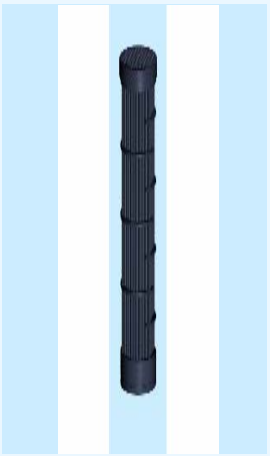
- A shell and tubes heat exchanger consists in:
  - A baffles cage
    - Baffles in ®Diabon N
    - Tie rods in ®Diabon NS
  - The ®Diabon NS1 or HF1 tubes
  - Two ®Diabon NS1 or HF1 tube sheets cemented to the tubes,



➔ DIABON® tube sheets are thick and sturdy

Shell

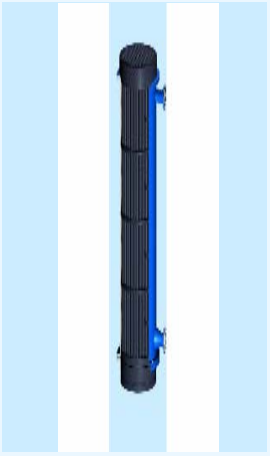
- A shell and tubes heat exchanger consists in:
  - A baffles cage
    - Baffles in ®Diabon N
    - Tie rods in ®Diabon NS
  - The ®Diabon NS1 or HF1 tubes
  - Two ®Diabon NS1 or HF1 tube sheets cemented to the tubes,
  - The shell, usually in carbon steel,
    - Gasket
    - O'ring gasket



➔ The O'ring gasket reduces mechanical stresses on the tube sheet.

Headers

- A shell and tubes heat exchanger consists in:
  - A baffles cage
    - Baffles in ®Diabon N
    - Tie rods in ®Diabon NS
  - The ®Diabon NS1 or HF1 tubes
  - Two ®Diabon NS1 or HF1 tube sheets cemented to the tubes,
  - The shell, usually in carbon steel,
    - Gasket
    - O'ring gasket
  - Bottom and top headers
    - PTFE gaskets



Complete heat exchanger

- A shell and tubes heat exchanger consists in:
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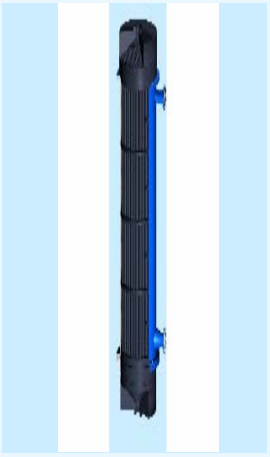
  - Two ®Diabon NS1 or HF1 tube sheets cemented to the tubes,
  - The shell, usually in carbon steel,
    - Gasket
    - O'ring gasket
  - Bottom and top headers
    - Unsintered PTFE gaskets
  - Steel plates
    - Pressure pads
    - Tie rods
    - Compression springs



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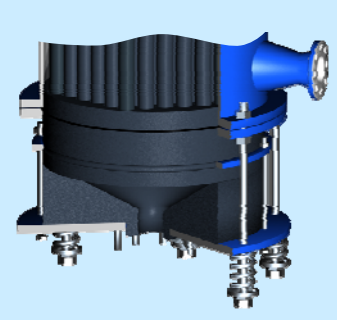
    - Gasket
    - O'ring gasket
  - Bottom and top headers
    - Unsintered PTFE gaskets
  - Steel plates
    - Pressure pads
    - Tie rods
    - Compression springs

Expansion system

- The expansion system is essential to compensate:
  - The effect of pressure on the tube bundle,
  - The differential expansion of the tubes versus the shell and maintain the tubes always under compression



Design data

Tube side	Shell side
Design pressure up to 16 bar	Design pressure up to 16 bar
Temperature up to 200°C	Temperature up to 200°C
Heat transfer areas up to 2000 m²	Different linings available
Tube lengths up 9 m	Steel in standard
Erosion protection possible	Other materials on request
	360° steam distributor possible
	Diameters up to 2.5m
	O-Ring comes in standard
	Other sealing on request

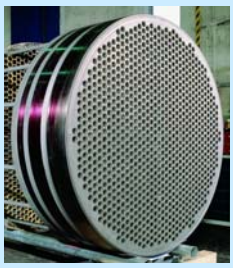
➔ Very versatile design

7. Design options

- Tube sheet reinforcement
- Headers design
- Shell variations
- Inlet nozzle variants
- O'ring design
- Erosion protection at inlet

Tube sheets reinforcement

- For phosphoric acid applications, especially when the tube sheet diameter exceeds 1200 mm, SGL CARBON recommends the carbon fiber reinforcement of the tubes sheets. The pretensioned carbon fiber is wrapped around the tube sheet in a way that brings:
  - Additional mechanical stability
  - Operational reliability
  - Increase equipment life time
- SGL carbon tube sheets are very thick (about 40% than those of the competition).
  - Significantly alleviate the risk of tube sheet cracking.



Carbon fibber reinforced tube sheet

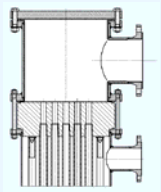
➔ DIABON® tube sheets are thick and sturdy

Headers designs

- For phosphoric acid applications, standard and extended headers are offered in:
  - High alloys such as S28 or G30
  - Carbon steel with rubber lining

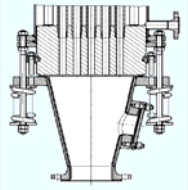
Rubber lined or massive high alloy headers

Rubber lined top header



- A Rubber lined top header can be used when:
  - The rubber can handle the corrosiveness and the temperature of the fluid

Rubber lined bottom header

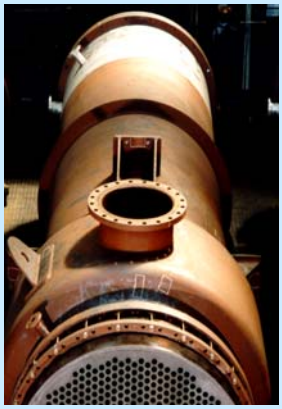


- A Rubber lined bottom header can be used when:
  - The rubber can handle the corrosiveness and the temperature of the fluid
  - Usually chloro- or bromo-butyls rubbers are the preferred lining materials in P_2O_5 applications

Rubber lined top header:
A manhole is possible on large diameters.

Shell variations

- Different materials are possible
  - Carbon steel is the standard
  - Stainless steel
  - Rubber lined steel
  - Phosphoric acid evaporators are usually designed so that the shell is in carbon steel and the lower 1,5 meters (5') is in stainless steel. UB6 or 316 L are usually chosen.

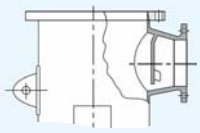


Carbon steel shell variations

Standard inlet nozzle

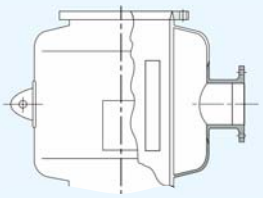
- Suitable for low steam flows
- Small evaporators

Steel shell with conical steam inlet nozzle



- Suitable for steam up to mid-size flows.
- The impingement plate
  - prevents tube erosion,
  - Reduces hammering risks

Steel shell with 360° steam distributor

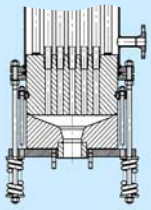


- Suitable for steam large flows.
- The 360° steam distributor
  - optimize the steam distribution,
  - improves the heat exchange efficiency,
  - prevents tube erosion,
  - reduces hammering risk

➔ **Optimal steam distribution prevents steam hammering**

Shell / Tube sheet sealing options

- SGL Carbon uses an EPDM O ring as a standard sealant between the shell and the floating tube sheet.
  - It allows an excellent gliding of the shell over the tube sheet
  - It has a proven reliability and offers a very long lifetime
  - Maximum temperature 180°C
  - Easy maintenance and repair
- Stuffing box is also possible on request



➔ **Reduced stresses on tube sheets**

Erosion protection at inlet

- SGL has developed two different technologies to prevent tube sheet erosion when products are particles loaded:
  - Ceramic coated inserts

Ceramic coated inserts

➔ **Technically proven solution: No tube sheet erosion**

8. Operational recommendations

- Heat exchanger sizing
- Steam quality
- Control valves
- Steam and condensates lines
- Start-up procedures
- Operations
  - Use of softening agents
- Cleaning
  - Chemical cleaning
  - Mechanical cleaning
- Equipment lifetime

Heat exchanger sizing

- Proper sizing is a key parameter to smooth and reliable operations.
  - Excessive fouling factors cause
    - Poor performances
    - Excessive fouling
- Acid viscosity is an important factor
  - Affects the film coefficient on process side.
  - Affects directly the heat exchanger surface area
- Neither aggressiveness nor conservatism are beneficial
  - Realistic fluids properties
  - Realistic fouling factors

Steam quality

- Steam usually comes from the sulfuric acid plant.
- Usually pretty clean
- Pressures between 4 (60 psi) and 10 bar (150 psi).
  - Desuperheating system might be necessary
  - Superheated steam
    - Reduces efficiency
    - Cause excessive fouling
- The steam usually contains a limited amount of non-condensables.
  - Must be removed occasionally during operation
    - Once a day
  - Systematically after start-up
    - Shell venting for a few minutes

Control valves

- On large units, two control valves in parallel are recommended
  - On large valve and one much smaller valve (half)
  - Progressive start-up
    - Small valve: opening 10 % per minute for 10 minutes
    - Main valve: opening 1% per minute until set point is reached
    - Prevent thermal stresses

Steam and condensates lines

- Extremely important for the reliability of the operations.
- Steam lines should be designed according to the rules, I.e.
  - Equipped with steam traps at the lowest points,
  - Equipped with filters,
  - Properly insulated.
- Condensates lines:
  - Proper removal of the condensates from the shell is a key factor
    - Prevents steam hammering.
  - Shall be biphasic at all times
  - Must be
    - Either vertical or sloped
    - Large enough
    - Never be horizontal nor climbing.
  - Shall be fitted with drain valves at the lowest points.

Start-up procedures

- Start-up is critical for the heat exchanger:

1. Axial pump must be started.
2. The condensate and steam lines must be totally drained.
3. The steam lines must be heated-up and drained.
4. Steam must be progressively introduced into the shell.
5. Set point can be reached within 30 to 50 minutes
   - The temperature difference shall not exceed 50ºC (100F)
6. The shell should be vented

Operations

- Monitoring
  - The pressure drop on process side
  - Overall heat transfer coefficient
    - Prevents the fouling gypsum layer to become too thick.
    - Determine with chemical cleaning is required
- The temperature difference should not exceed 25ºC (50F) to 30ºC (60F)
  - Prevents too rapid fouling.
- The temperature difference between inlet and outlet should be roughly 3 to 5ºC.
  - Prevents too rapid fouling.
- Use of softening agents
  - Sodium TriPolyPhosphate (STPP) has given interesting results.
  - Results may vary with rock used and process conditions.

Cleaning

- Chemical cleaning:
  - Most recommended cleaning
  - Several advantages over mechanical cleaning
    - No need to disassemble the equipment.
    - Can be very efficient if made early enough
    - Slows down the fouling during the next production cycle
- Chemicals
  - Hot water,
  - Diluted sulfuric acid,
  - Fluorhydric acid,
  - Chelants
    - EDTA (ethylenediaminetetraacetic acid)
    - SS'-EDDS (S, S'- ethylenediaminedisuccinic acid)
  - Impurities can severely affect the crystal structure of gypsum.

Cleaning

- Mechanical cleaning:
  - Mechanical cleaning is widely used around the world
  - Aggressive methods for the graphite tubes
    - Use of self-progressing rotating water jet low pressure blasters (maximum 200 bar, 3000 psi) mounted on a flexible hose
    - High pressure non-rotating water blasters mounted on lances is to be totally banned.
    - Only to be performed by an experienced crew.

Equipment lifetime

- Experience shows that equipment lifetime depends mostly on the operation conditions.
- Lifetime of 12 to 15 years in operation is commonly achieved. After that time, the need for unscheduled maintenance is likely to increase exponentially.
- DIABON® heat exchangers that have been sold in the early 1980's with carbon fiber reinforced tubes are still nowadays in operation with a limited number of broken tubes.

8. Graphite versus nickel alloys

- The Floridian phosphate exception
- Actual pricing
- Comparative advantages
- Experience

Graphite versus nickel alloys

- Floridian phosphate has very low halides content.
  - Exception
  - Use of nickel alloys for the 1st and 2d stages of evaporation is possible.
  - For the 3rd stage, only carbon fiber reinforced tube are used in Florida also.
  - Life expectancy of a nickel alloy evaporator rarely exceeds 5 to 6 years.
  - The alloy heat exchanger last about 40% of the life expectancy of its graphite counter-part.
- At today nickel price, a nickel alloy phosphoric acid evaporator costs roughly 30 to 50% more than a graphite shell and tube exchanger with carbon fiber reinforcement.
- Nickel alloy evaporators are more forgiving from a mechanical standpoint. They accept generally better process and service offsets. On the cleaning side, they allow high pressure water jet blasting
- Nickel alloy evaporators are not at all forgiving on the chemicals standpoint.
  - Chemical cleaning limited: use of sulfuric acid not recommended
  - The use of chelants is to be banned.

Graphite versus nickel alloys

- A well known phosphoric acid producer located in the middle east, implemented 3 large alloy G30 phosphoric acid evaporators in 1996. After 5 years of operation, the three heaters where totally corroded, principally at the welds (tube / tube sheet, longitudinal weld on the tube). 30% of the tubes were plugged and new tubes were bursting every days…
- All the three units were replaced in 2001 by carbon fiber reinforced graphite tubes evaporator from SGL CARBON. So far, no tube out of 2697 have cracked.
- It is to be mentioned a very specific attention has been paid to the steam and condensates lines and that all the start-up, operational and shut-down procedures have been totally computerized to prevent human errors.

9. Conclusions

- Advantages of carbon fiber reinforced graphite
- Importance of smooth operations
- Importance of cleaning procedures
- Best possible design
- Contact information

Conclusions

- SGL CARBON's Carbon fiber reinforced synthetic resin impregnated tubes bring a lot of additional reliability to operations.
- Improvements are particularly significant when the steam and condensates systems are not properly designed or harshly operated.
- Today, nearly all large phosphoric acid evaporators in DIABON® graphite are supplied with carbon fiber-reinforced tubes and tube sheets.
- Industrial experience shows with HF1 tubes are implemented, when the steam and condensate lines are properly designed, and when start-up and shutdown procedures have been totally computerized, it is possible to achieve a zero failure rate for the first 5 years of operation at least.
- Quality of the steam, the way steam and condensates piping network are designed, and moreover the way the evaporation units are operated are of primary importance for the reliability of the operations.

Conclusions

- The use of adapted mechanical cleaning procedures is essential to enhance equipment lifetime.
- The use of chemical cleaning instead is recommended.
- The use of chelants such as SS'-EDDS can give astonishing results.
- The adding of softening agents, such as STPP, to the evaporation loop can give interesting results
- Best possible graphite heat exchanger design:
  - Carbon fiber reinforced tube sheets,
  - A 360° steam distribution,
  - Carbon fiber reinforced tubes,
  - Graphite baffles,
  - and ceramic coated inserts.

Thank you for your attention

- **Question are welcome.**
- **Contact information:**

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