SGL CARBON GROUP

Strongsville
25 April, 1997

Carbon Fiber Reinforced Graphite Tubes in Phosphoric Acid Evaporation

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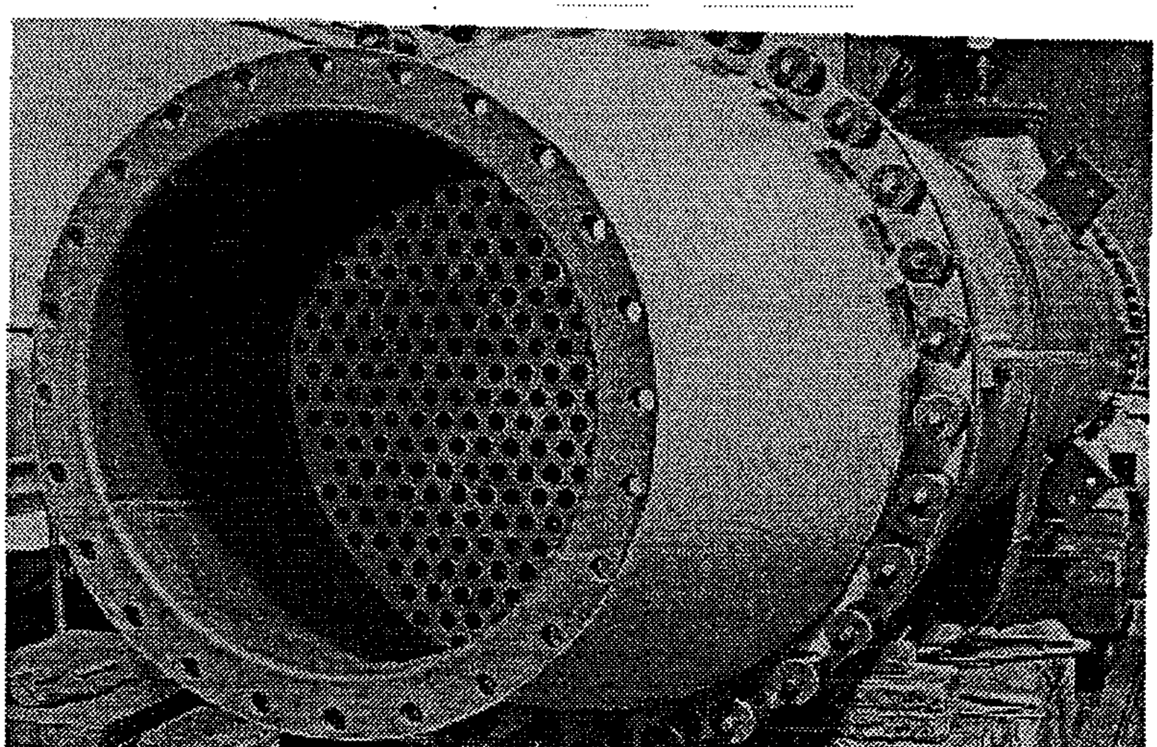

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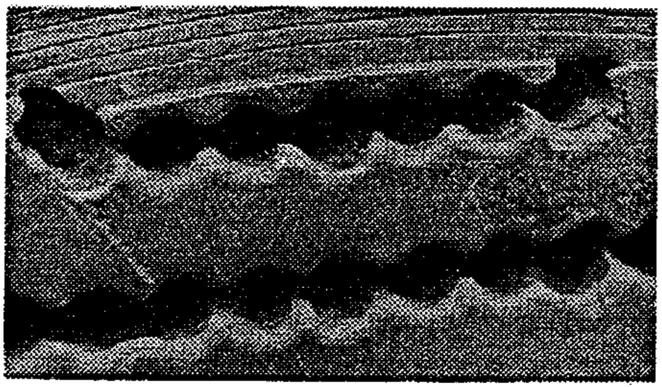
Graphite is used as a material for phosphoric acid evaporators because of the excellent corrosion resistance and good heat transfer rate. Mixed results have been experienced for resistance to mechanical damage. The harsh nature phosphoric acid evaporation can create a number of failures in graphite equipment. The pictures below show a few examples of these mechanical failures.



erosion of a block exchanger

tube breakage of a shell and tube

Graphite equipment failure can be attributed to many different root causes (fig. 1).

Reasons for graphite failure

		tubes	Graphite tube sheets	blocks
Manufacturer & Repair Shop	Poor impregnation	√	√	√
	Incorrect strength calculation	√	√	√
	Equipment is not designed to account for material properties	√	√	√
	Assembly errors		√	√
	Poor cemented joints	√		
Operation	Pressure shocks (steam hammer)	√	√	√
	Exceeding material max. temp.	√	√	√
	Poor condensate drainage	√		√
	High acid velocity (erosion)		√	√
	Excessive encrustation and blockage	√		√
	Start-up and shut-down procedures that are too strenuous for graphite	√		√
Cleaning & handling	Lack of caution high pressure water cleaning	√		√
	Incompatible chemicals used for cleaning	√	√	√
	Excessively high torque on bolts	√	√	√
	Misc. mechanical damage		√	√

Figure 1 (Reasons for graphite failure)

Tube failure or block crack results in a plant shut-down, loss of production, and acid contamination of the steam condensate. Additional significant repair and labor costs are usually associated .

This paper will describe methods that can be used to insure the minimum number of failures in graphite equipment with an emphasis on carbon fiber reinforced tubes.

Impervious graphite manufacturing process, mechanical and physical properties

The manufacturing steps for producing graphite are illustrated in figure 2. The most important steps for ensuring quality are the selection of the raw material, mixing, molding, baking, graphitization, and impregnation.

Chemical properties

Chemical resistance is the most common reason for the use of impervious graphite equipment in industry (fig. 3).

FLUID	CONC.	TEMP.
Inorganic Acids		
Hydrofluoric acid	0-60%	boiling
Phosphoric acid	all	356°F
Hydrochloric acid	all	boiling
Sulfuric acid	0-70%	boiling
Sulfuric acid	70-80%	356°F
Sulfuric acid	80-96%	356-45°F
Organic Acids		
Chloroacetic acid	all	all
Acetic acid	all	boiling
Sulfonic acids	all	356°F
Salt solutions		
Acetates, Chlorides, Fluorides, Sulfates, Sulfites	all	356°F
Calcium hypochlorite	all	
Sodium hypochlorite	all	
Various Substances		
Hydrogen chloride, gaseous	100%	356°F
Hydrogen fluoride, gaseous	100%	356°F
Sulfur dioxide, gaseous and liquid	100%	356°F
Organic Compounds		
Chlorobenzene, Dichlorobenzene	100%	356°F
Cyanogen chloride, Cyanuric chloride	100%	356°F
Halogenated hydrocarbons	100%	356°F
Mixture of Substances		
Calcium bisulfite solution (pulp dig. liquor)	all	356°F
Hydrochloric and sulfuric acid (pickling)	all	boiling
Sulfuric acid (spin bath solutions)	all	boiling

Fig. 3 Corrosion resistance of graphite

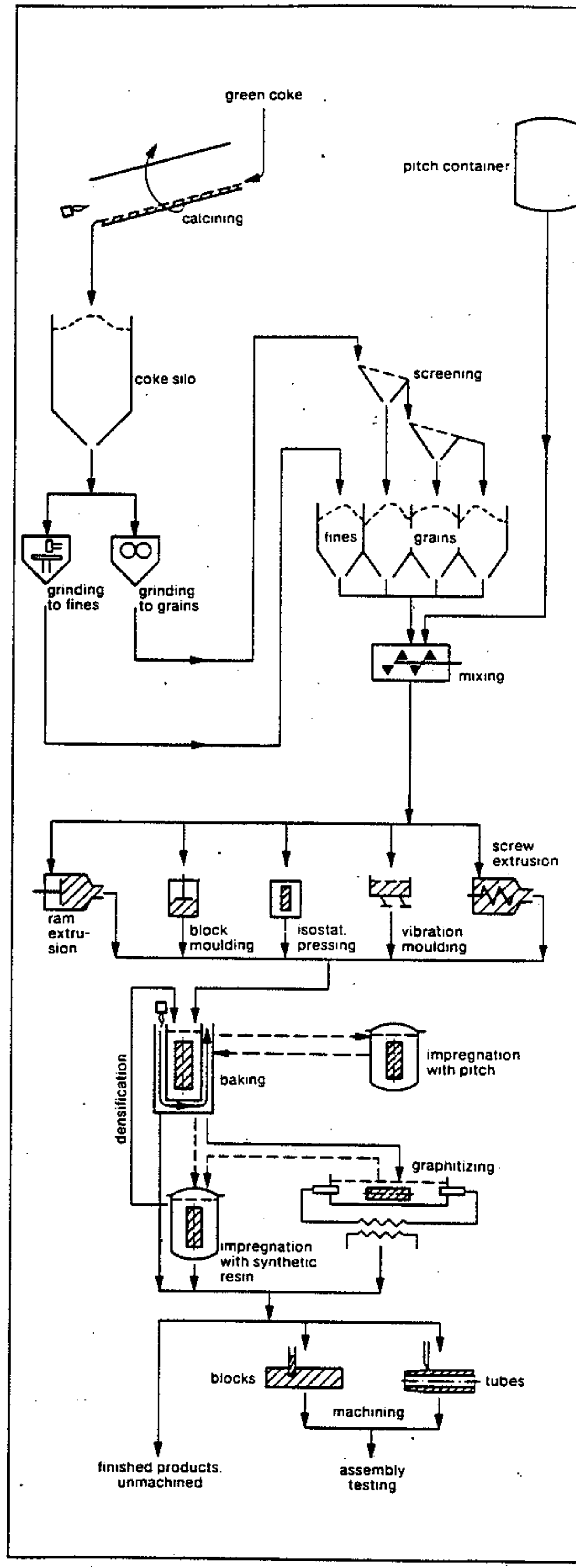


Figure 2

Methods that the equipment manufacturer and the repair shop can use to improve evaporator performance.

Material selection

The correct material grade must be selected for the graphite heat exchanger components. Material strength, pore size, pore distribution, grain size and suitability for resin impregnation are factors that must be carefully considered.

Resin impregnation

Corrosion resistance, strength and maximum operating temperature are determined by proper impregnation of the porous graphite material with synthetic resin. Resin properties, details of the impregnation process, and the curing parameters all have an impact on the corrosion resistance of the final product. The quality of the impregnation will best be seen in a micrograph.

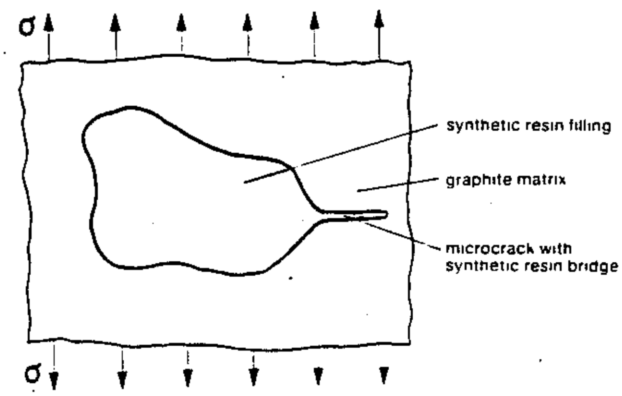


Figure 5

The resin must link to the graphite matrix, therefore no gap should exist between pore wall and the resin. A correct impregnation will increase the strength of the material increases by a factor of 2 to 3 (fig. 5). Selecting the right graphite material combined with the proper impregnation results in the best mechanical strength and corrosion resistance.

Joining technology

Graphite parts must be joined together by using a cement consisting of graphite powder and resin. The joint factor depends on the thickness of the cemented joint. The optimum thickness for DIABON material is 0.007" (fig. 6). This optimum can change with other graphite grades.

Graphite is suited for phosphoric acid applications at any concentration up to the maximum allowable operating temperature for graphite material. The chlorine and fluorine content in the acid does not affect the impregnated graphite.

Physical properties

Shown below in figure 4 are four graphs showing important mechanical and physical properties of graphite.

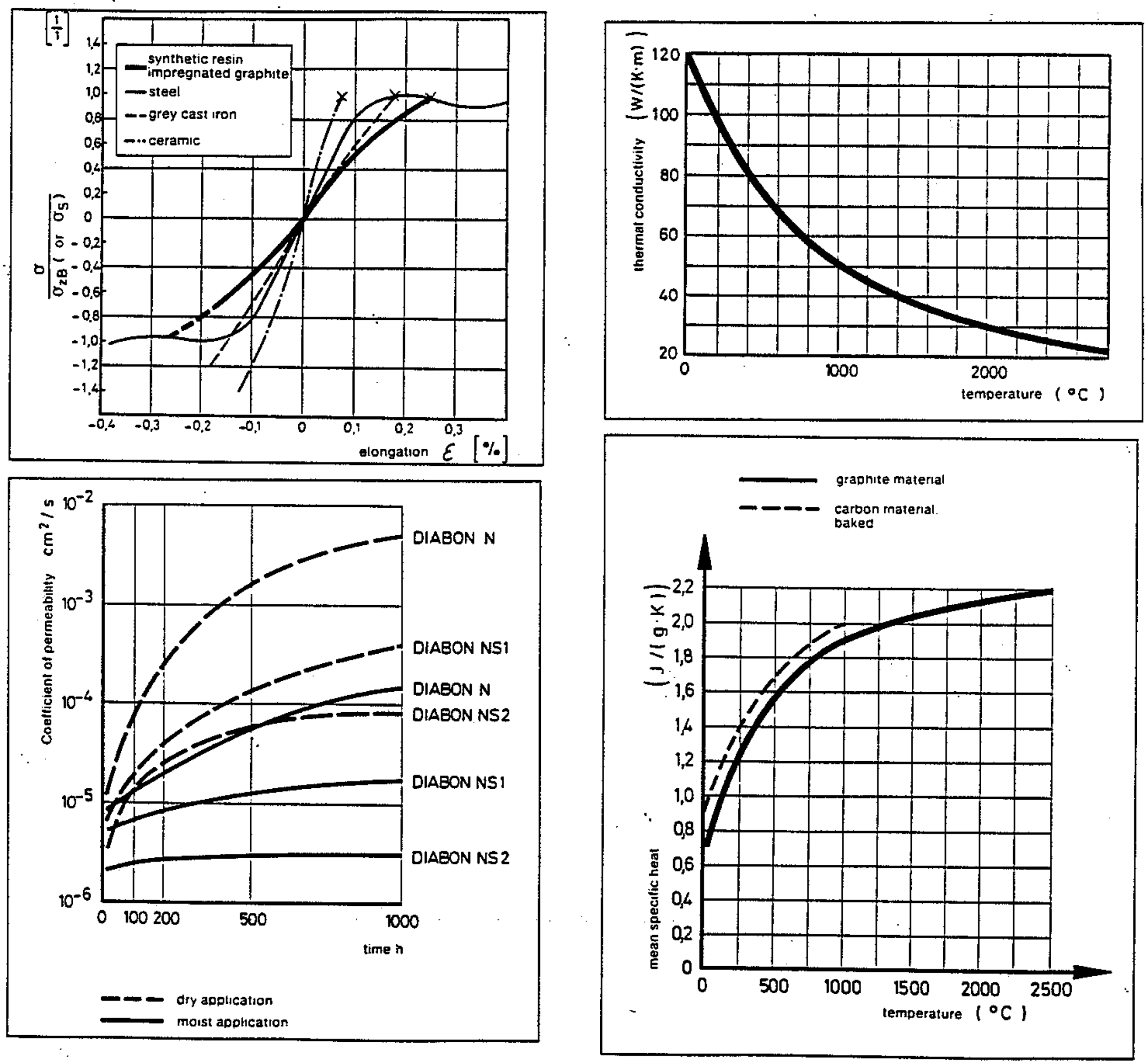


Figure 4

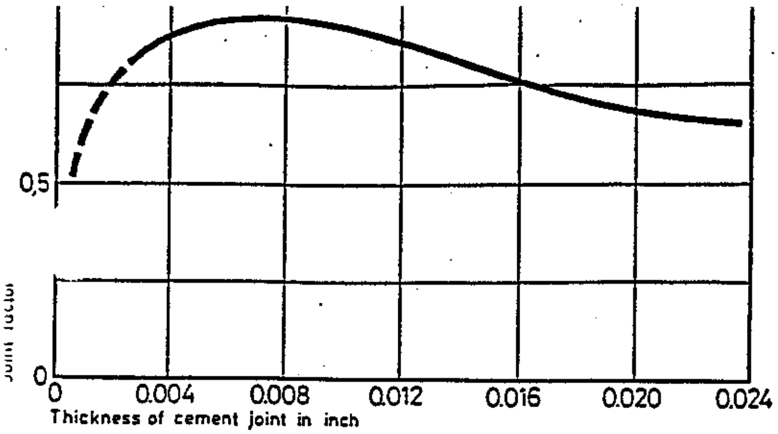


Figure 6

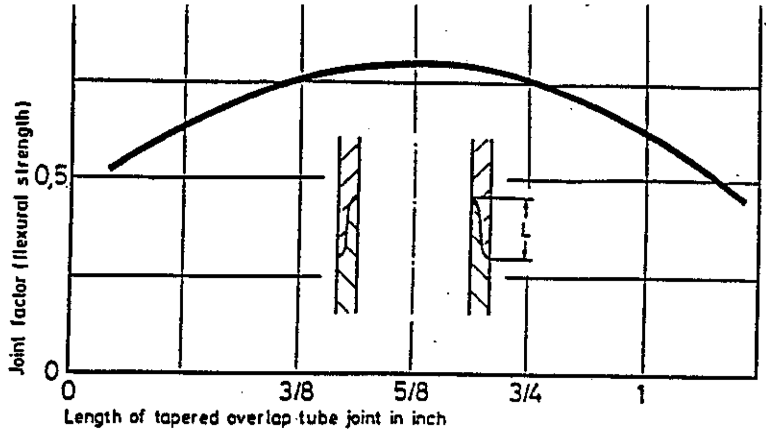


Figure 7

The quality of tube/tube joints is also influenced by the shape of male/female connection and length of the overlap (fig. 7).The development of the optimum joint tube/tube sheet is shown below (fig. 8-10).

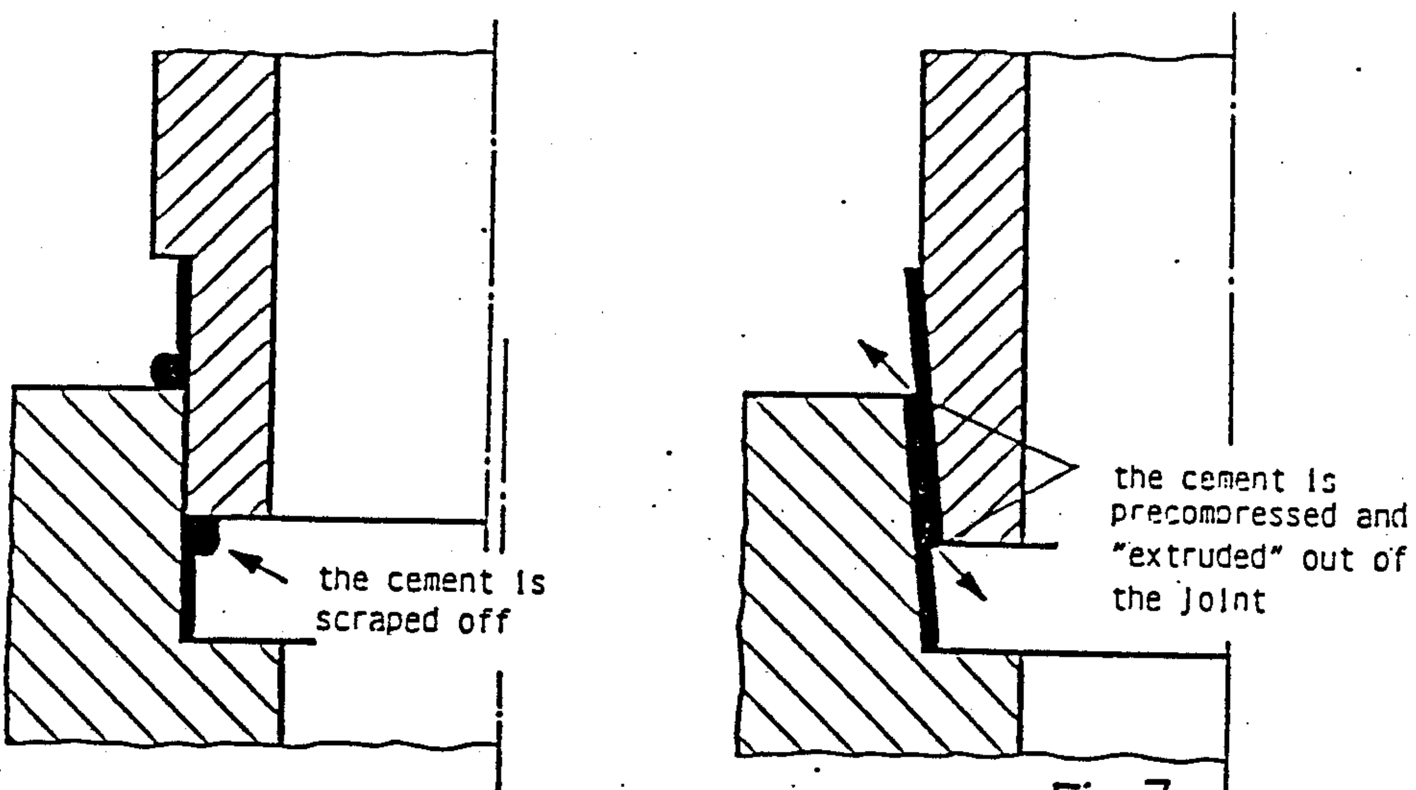


Fig. 7

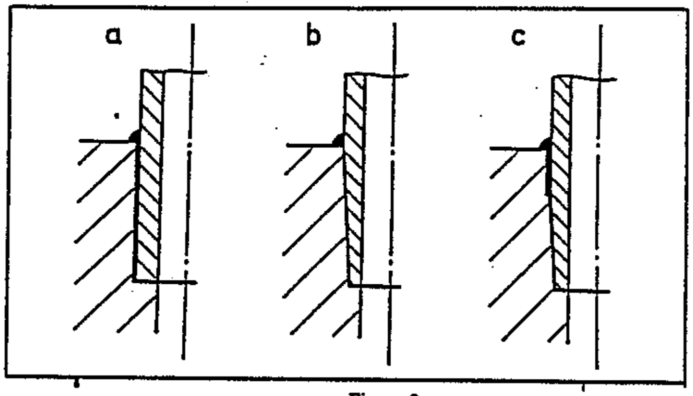


Figure 9

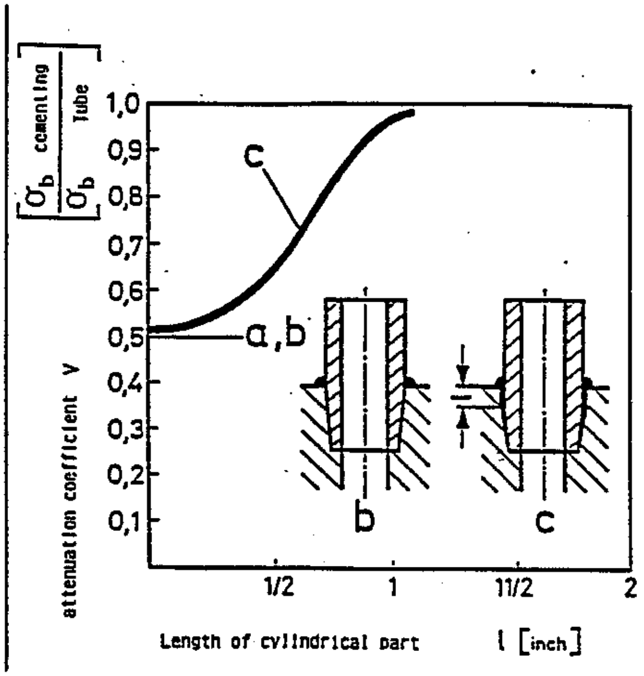


Figure 10

Design a) results in a low flexural and tension strength and possible leakage of the joint after assembly.

Design b) is a better solution because the cement is compressed and the excess cement is forced out of the joint.

Design c) is a exclusive shape of SGL and has a tapered end and a cylindrical section. The conical part of the joint compresses the cement and the joint thickness is controlled. The cylindrical surface of the tube end is prepared to avert any bond of the cement to the tube. It is only supported by the cement. Any shrinkage stress of the cement as well as stress peaks on the tube to tube sheet transition is avoided. Therefore the flexural strength of the joint increases to approximately 90% of the tube strength.

Special Performance Enhancing Products

Carbon fiber reinforced graphite tubes (DIABON® HF1)

Graphite is a fragile material with a low breaking elongation of approximately 0.2%. Carbon fiber is an excellent material for reinforcement of graphite for the following reasons:

- very high modulus of elasticity
- very high tensile strength
- very low coefficient of thermal expansion
- identical corrosion resistance as graphite

The DIABON® HF1 tube is a standard DIABON® (impervious graphite) tube wrapped with carbon fiber under tension (fig. 11)

Figure 11

Illustrated below in figure 12 are three different types of tubes that have failed. The glass and standard impervious graphite tubes have failed in a manner that would cause a significant amount of acid to enter the condensate. The DIABON® HF1 tube has only a tiny crack that is barely visible. This type of crack will only release small quantities of acid into the condensate. The failed wrapped tube will actually contain the process fluid at 40 to 50 psi without leaking any acid, as demonstrated in figure 13. This figure demonstrates how a fiber wrapped tube that has failed would behave if the air on the inside were pressurized to 140 psi.

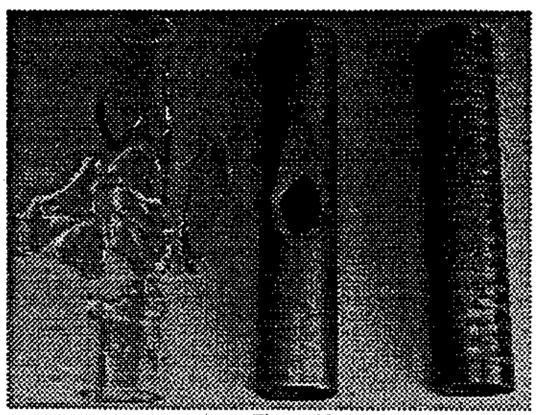


Figure 12

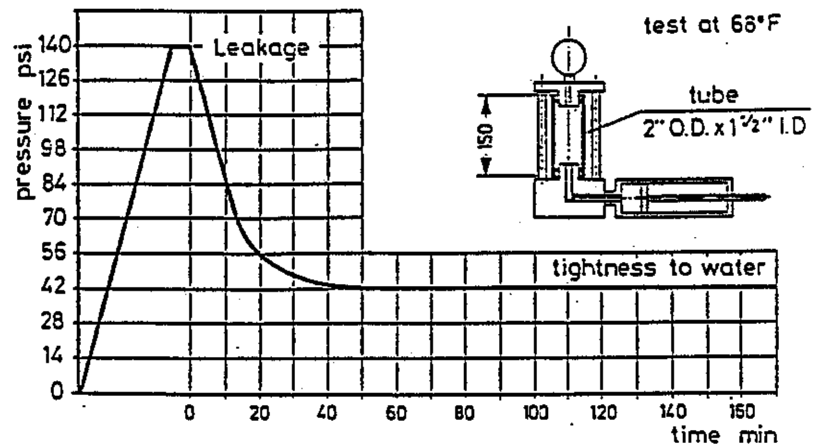


Figure 13

The tube ends and the tube to tube joint have additional reinforcement to further increase the strength of these areas. Due to the fact that the carbon fibers have a negative coefficient of thermal expansion, the compression on the tube increases as the temperature increases. This behavior will allow the bursting pressure of the fiber wrapped tube to increase at higher temperatures, where this property decreases with temperature for standard tubes. The DIABON® HF1 tube is comparatively 2.5 times more resistant to steam hammer than a standard impervious graphite tube. With a bursting pressure that is nearly 40 to 50% higher than standard tube, the DIABON® HF1 tube offers significantly more insurance against pressure spikes. The properties of the DIABON® HF1 tube are compared to a standard DIABON® tube in table 1.

The heat transfer coefficient of a phosphoric acid evaporator with wrapped tubes would theoretically be approximately 5% lower than the same evaporator with standard tubes. Comparisons of heat transfer actually occurring in the field have shown that there is no appreciable difference in performance.

GRAPHITE TUBES 2" O.D. x 1 ½" I.D. Resin impregnated Physical properties	Units	DIABON® NS1 (standard tube)	DIABON® HF1 (fiber reinforced)
Flexural strength	psi	7250	8700
Bursting pressure @ 68°F Bursting pressure @ 302°F	psi psi	1070 1000	1425 1565
Resistance to mechanical damage	relative %	100	250
Leakage pressure of a cracked tube water pressure inside tube	psig	0	142
Thermal conductivity	BTU/ft/hr/°F	48.4	29
Maximum operating temperature	°F	356	356
Flexural strength of tube to tube joint	psi	5800	8000
Flexural strength of tube to tube sheet joint	psi	6525	8000

Table 1

If a fiber wrapped tube experiences a failure. The small amount of leakage that may occur from the broken tube will allow the evaporator to continue to operate without interruption until the next scheduled plant shut-down. The cracked tubes may be replaced individually or the bundle may be completely retubed. The HF1 tube bundle can be cut with a saw. Undamaged parts of tubes can be joined. A layer of carbon fiber tape is applied to each end of the cut tube secures that fiber wrapping and insures that the fiber on the tubes will not unwrap.

Reinforcement of tube sheets and exchanger blocks

All tube sheets and exchanger blocks should be manufactured from a monolithic piece of graphite to avoid cemented joints which will reduce the mechanical strength. A large graphite part can crack if various factors occur simultaneously. Investigations revealed that tangential stresses are the cause of nearly all cracks that occur in these parts. The carbon fibers that are wrapped around the circumference of the part will counteract these stresses and prevent cracking. (fig. 14)

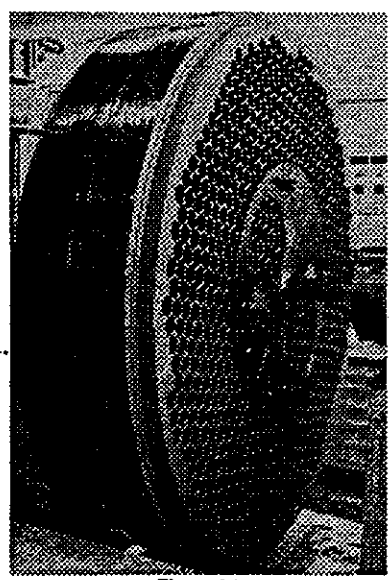


Figure 14

Wear protection for graphite evaporators

Erosion of the tube sheets and blocks can occur due to the high velocities of solid particles contained in the phosphoric acid. Many processes use elevated acid velocities to reduce scaling of the heat exchanger. A wear resistant coating (ex. ceramic oxide) and an optimized flow geometry at the inlet and outlet will increase the lifetime of the graphite parts. (fig. 16 & 17)

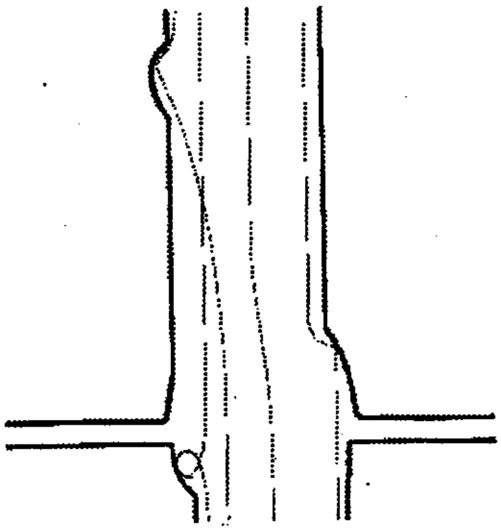


Figure 16

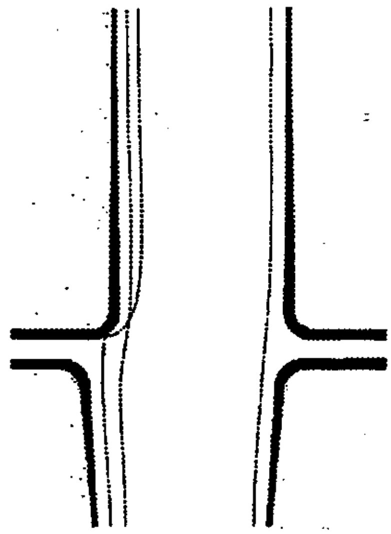
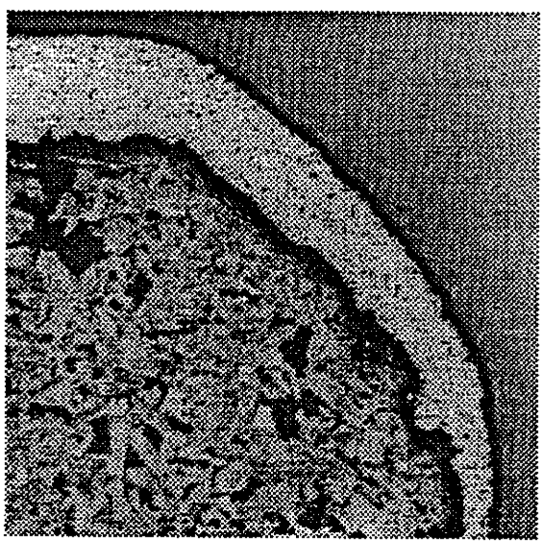


Figure17

Shell and tube heat exchangers only require the inlet face of the tube sheet to be coated. Block heat exchangers must have both faces of each block coated due to the gap between the holes and the machining tolerances of the holes. The coating that is used must be chemically resistant to the process fluid and does not reduce the heat transfer rate of the heat exchanger. Shown below in figure 18 is a micrograph of a correctly applied ceramic oxide coating.



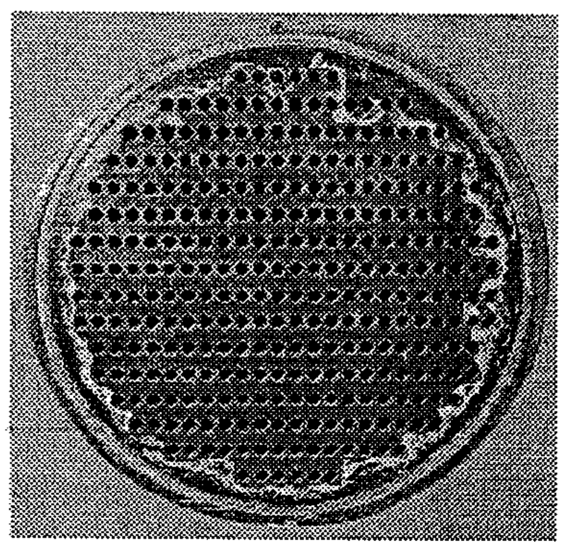


Figure 18

Removal of encrustation

Encrustation of the heat exchanger tubes has always been a problem in evaporator operation. The capacity of the evaporator decreases, the pressure drop increases and mechanical failure can result under certain circumstances. The maximum thickness should not exceed 1/8" to insure that the factors above do not adversely affect the heat exchanger performance.

a) *Removal with hot water* - This is a simple method that can be used successfully if the encrustation is relatively thin and soft. The water velocity in the tubes should be as high as possible (more than 9 ft/s).
b) *Chemical cleaning* - Since impervious graphite is resistant the corrosion that many powerful cleaners can cause, a suitable chemical cleaner will usually be available. Consult published corrosion resistance charts for impervious graphite or consult the manufacturer before using a chemical for cleaning.
c) *Cleaning with high pressure water* - Graphite tubes can be cleaned with high pressure water up to a maximum of 4000 psi. At this pressure the water will already begins to erode the graphite. Misapplication of this cleaning method accounts for a high percentage all tube breakage. The water pressure, the system, and the handling must be carefully selected for this application. Nozzles that are connected to a solid pipe can be rammed into the tube and cause severe damage. A self-propelled nozzle with a flexible hose will prevent the nozzle from being rammed into the holes. (fig. 19)

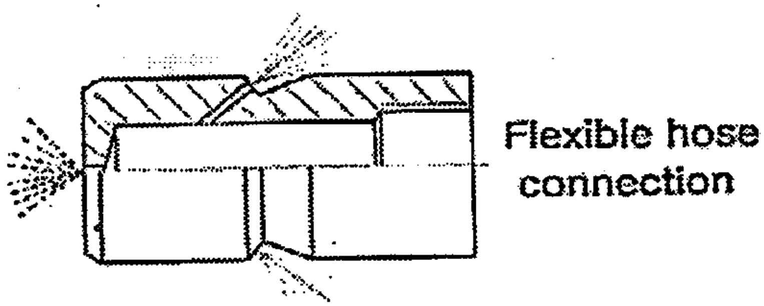


Figure 19

SUMMARY

Graphite offers one of the most economical solutions to the corrosion problems present in phosphoric acid evaporators. The disadvantages associated with the mechanical weakness of graphite can be minimized by the following methods:

- selection of a suitable grade of graphite
- stabilized impregnation
- proper mechanical design of the equipment

Carbon fiber reinforcement and wear resistant coatings on the face of the blocks and tube sheets, are two special products that SGL Technic can provide to enhance the mechanical strength of the graphite. The performance of DIABON HF1 tubes have been proven in many phosphoric acid evaporators around the world. A heat exchanger equipped with fiber wrapped tubes would require a 15 to 25% additional capital investment that will be returned quickly with reduced downtime and maintenance costs. With these products and the methods described above the reliability and life of the phosphoric acid evaporator.