

Carbone Lorraine

Graphilor® 3

The high-end impregnated graphite

CARBONE LORRAINE

Dedicated Innovation, Dedicated Partner

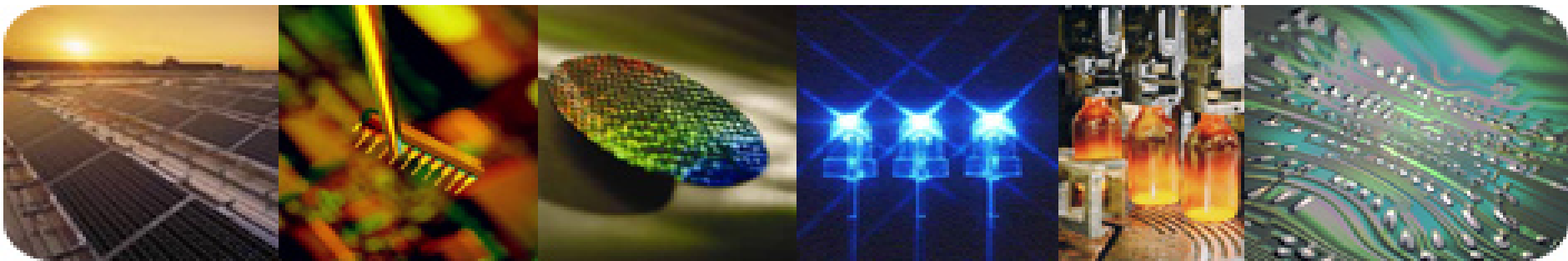


- Graphilor® 3

- Graphite manufacturing process
- Graphite transformation into Graphilor® 3
- Applications

CL offers ultra-pure graphite for high-end applications

- The Group Carbone Lorraine produces an ultra-pure grade of graphite providing **optimum resilience to extreme temperatures** (up to 3,000°C).
- High-temperature applications for ultra-pure graphite:
 - Key material for the production of silicon
 - Used throughout the semiconductor production chain
 - Used to design fabricated solutions for the plastics, glass and metal-working industries, as well as for furnace linings.
- Carbone Lorraine Chemical Equipment is the sole manufacturer to systematically use isostatic graphite for producing their impervious graphite equipment



Graphilor® 3, the highest impregnated isostatic graphite with ultra-fine grains

- Graphilor® 3 is CL's trade mark for impregnated graphite, resulting from the combination between ultra-fine grain graphite and specific resin
- CL has developed a specific know-how for their impregnation process over the last 50 years.
- CL Chemical Equipment Division uses Graphilor® 3 to manufacture all their process equipment such as heat exchangers, columns, synthesis units, bursting discs...
- Key advantages of Graphilor® 3:
 - High resistance to corrosion
 - Resistance to temperature and thermal shock
 - High mechanical resistance

- Graphilor® 3

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Raw materials



■ Coke

- By-product of oil or coal distillation
- During distillation, **pitch** (tar) is generated. It is then **carbonized** (at more than 1,000°C) to produce **coke**.



■ Binders

- **Pitch** is used as a **binder** to stick the coke particles together.
- **Coal pitch** gives a higher carbon content after carbonization.



■ Carbon black/ Natural graphite

■ Raw materials are inspected upon reception:

- Ash
- Moisture
- Volatile matter
- Melting point for binders

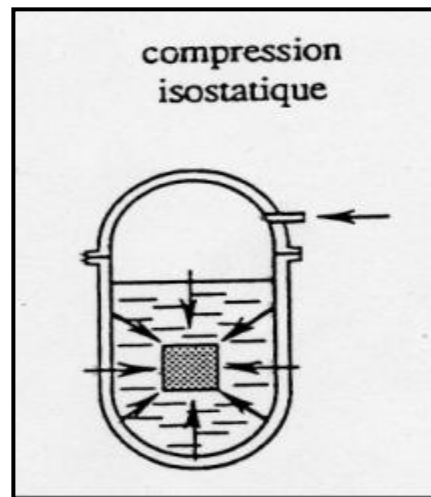
Grinding & Blending

- Grains are milled to the right grain size using roller mills.
- Mixing process:
 - **Ingredients** (coke, graphite and binder) are loaded into the **mixer**.
- Mixing is performed at a high temperature
 - the pitch melts and moistens the grains
 - Viscosity increases from paste to solid state

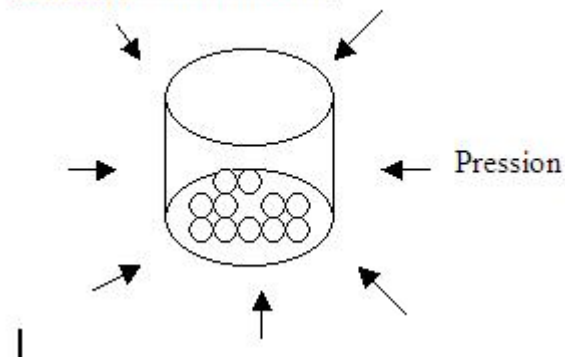


Grinding & Isostatic pressing

- Grinding : the mix is milled in a hammer mill in order to avoid grain separation
- Isostatic pressing
 - The mix is loaded into a rubber mold and agitated to allow perfect filling
 - **The mold** is placed in an **isostatic press where very high pressure** is applied up to 700bars
- The result is an homogeneous material with ultra-fine grains of carbon

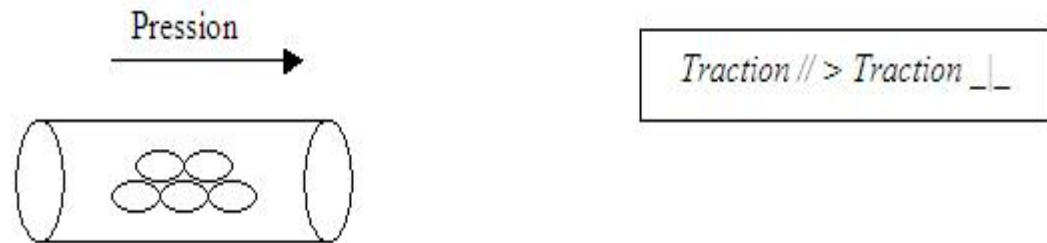
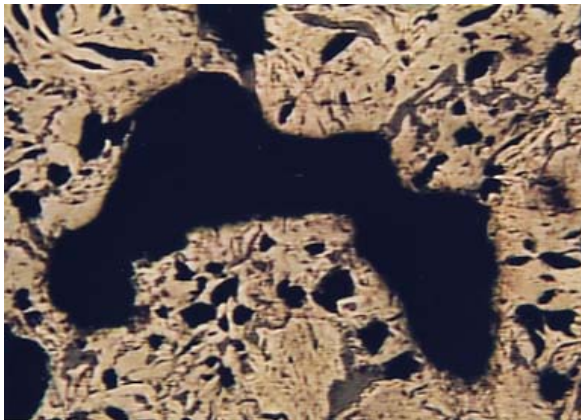


Isostatic Compression :



Extrusion, the alternative process for the graphite manufacture

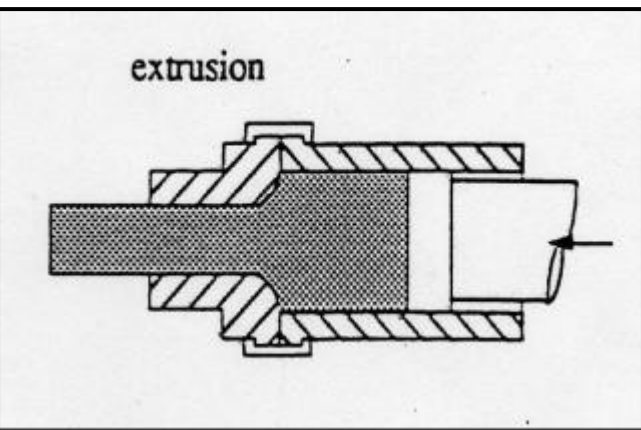
- The field applications of extruded graphite do not require high mechanical properties and low porosity (see below picture) on the opposite of isostatic graphite
- Extruded graphite is generally used for producing electrodes for metallurgy



The other suppliers of graphite equipment use extruded graphite as their raw materials

CL Graphite extruded tubes

- CL graphite tubes are manufactured by an extrusion process, up to 6 meters without a join
- CL graphite tubes have the same properties as ultra-fine grain isostatic rods
- To enhance higher performance material, CL has mastered in-house all the production stages specifically :
 - Baking
 - Graphitization



Baking

- The purpose of baking is to remove the volatile compounds and produce amorphous carbon.
- The furnace is loaded with wagons or by fork trucks. The heating time is very long to enable all the volatile matter to be removed from the blocks without cracking.



■ Cycle time: 1-2 months ■ Temperature: 800°C – 1,000°C

Graphitizing & Machining

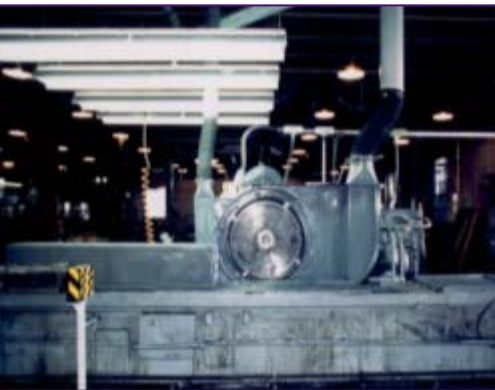


- Graphitization transforms amorphous carbon into artificial graphite:
 - Blocks are graphitized at very high temperature
 - They are covered by coke powder for oxidation protection and insulation



- After graphitization, thermal conductivity is significantly improved

■ Cycle time: 1-2 months ■ Temperature: 3,000°C.



- Machining : Raw blocks are sawn to final dimensions.

Testing of graphite and shipment

- Apparent **density** (100% testing).
- **Resilience** (100% testing).
- **Flexural strength** (by sampling).
- **Ultrasonic checking** (100% testing).
- **Rockwell** hardness (by sampling).
- **Shore** hardness (for mechanical grades only).
- **Ash** content (by sampling).
- **Coefficient of Thermal Expansion** (100% testing; per graphite parts to be SiC coated).
- Each block is engraved to have full traceability before shipment



CL graphite manufacturing plant in China – The Chongqing plant

- Duplication of St Marys (USA) factory
 - The plants boasts both a highly favorable cost base and
 - high-end product quality based on CL know-how
- 4 unique strengths
 - Graphite production know-how from CL St Marys
 - Large production capacity
 - Large diameter graphite blocks
 - Sole isostatic graphite producer in China

Key figures

- Facility surface area 62,000m²
- Production capacity: 3,500t in 2009, 5,000 tonnes in 2010
- Employees: 80 people presently – 160 eventually



CL isostatic graphite

Properties

	Extruded graphite Fine grain Grade S			Isostatic graphite Ultra-fine grain Grade X
Dimensions (mm)	$\emptyset \leq 450$	$450 < \emptyset < 900$	$900 \leq \emptyset$	$900 \leq \emptyset$
Mean grain size (μm)	220	360	360	20
Density	$D > 1.7$	$D > 1.56$	$D > 1.60$	$D > 1.75$
Porosity %	14 – 18	15 – 20	20 – 25	12 – 15
Mean pore diameter (μm)	5	8	9	1.7
RF // (Mpa)	15 -20	12 – 18	10 – 12	< 25

CL isostatic graphite

Key features & benefits

Key features

Customer Benefits



*Carbone Lorraine
Ultra-fine grains
graphite*

- Smaller porosity
- Higher mechanical resistance

Higher lifetime
High-end solution
Compact equipment
(high exchanger are
 $\text{m}^2/\text{graphite volume m}^3$)

- Production in USA and China

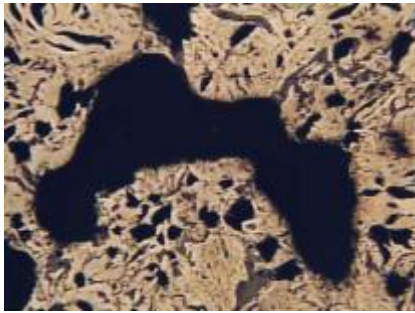
Large production capacities
Close to customers
Shorter delivery times

Contents

- Graphilor® 3
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2 reasons why transforming graphite into Graphilor 3

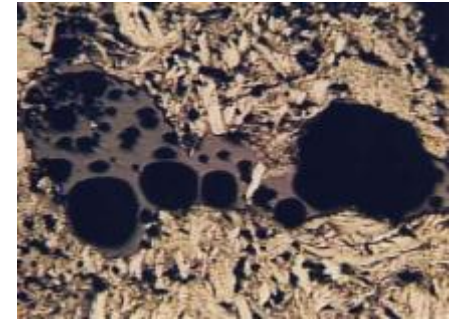
Isostatic
graphite



+ *Specific resin
impregnant*

*(Impregnation
process)*

= Graphilor® 3



Graphite Strengths

- Excellent conductivity
- Excellent corrosion resistance
- Good Mechanical resistance

Graphite Weaknesses

- Porosity



Graphilor® 3 Strengths

- Excellent conductivity
- Corrosion resistance depending on the selection of impregnant
- **Air tightness**
- **Reinforced mechanically**

Stages of graphite transformation into Graphilor® 3

- Stages of the graphite transformation into Graphilor® 3
 1. Machining & drilling
 2. Impregnation to ensure air tightness
 3. Final machining
 4. Cleaning
 5. Tests

- All these steps can be achieved in :
 - France
 - UK
 - Morocco
 - India
 - China
 - USA

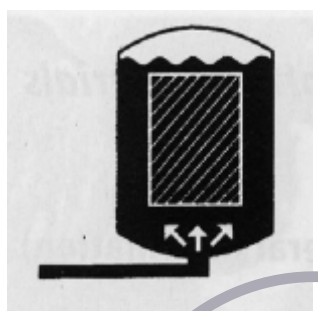
Machining & drilling before impregnation



- Machining of graphite rods or squares in order to obtain graphite blocks or tubesheets
- Drilling of blocks or tubesheets up to 90" with multi-head drilling tools
- Holes drilling from 8 mm to 35 mm diameter for blocks and from 3/4" to 2" diameter for tubesheets.



Impregnation process

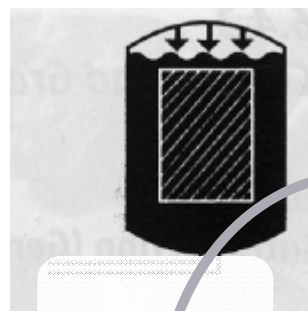


2 Suction of resin

- Through the depression occurred by vacuum

- Resin is penetrating the pores

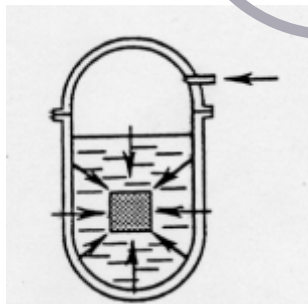
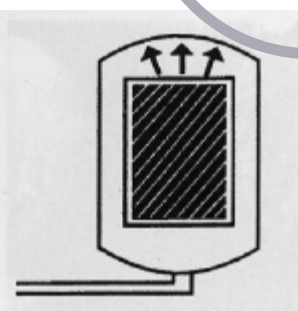
3 Pressurize the vessel



4 Remove the resin

- Polymerization of the resin in the graphite

5 Baking of vessel



End Machining after impregnation

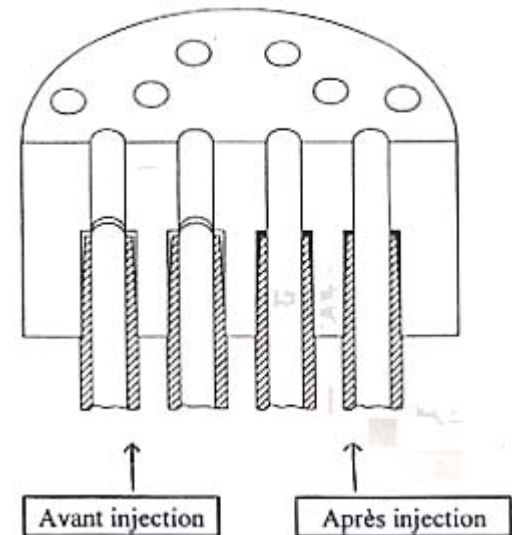
Blocks

- End machining to the final dimensions
- Gasket Sealing area machining
- Graphite baffle cementing



Tubes

- Cut to the dimension.
- Bond together with AN cement if the required length of the tube is more than 6 meters
- Machining of tubes ends before cementing to the tube sheet



New development : cleaning for tubes

- CL carried out tests early in 2009 on existing machinery to clean the tubes both internally and externally
- CED has now a new fully automatic brushing machine and can now propose the cleaning step as a standard for all tubes
- **Features** : better visual aspect & improvement to the thermal conductivity



Tests on impervious graphite

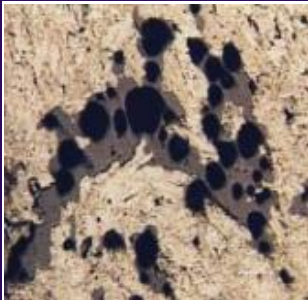
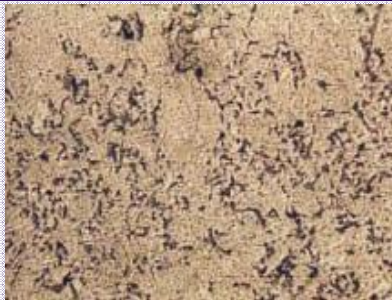


Tightness tests 100% control

- Blocks BS, XBS & XC and XBS Tubes are controlled **@9bar** air under water => highest control level
- Blocks XTH are controlled @6bar air under water
 - Full tightness is guaranteed by CL
- Tubes XBS are controlled @20bar water under water (mechanical) and 9 barG (tightness)

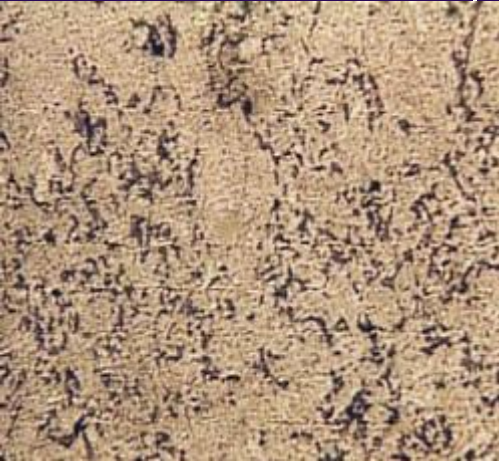
Statistic tests

- Blocks
 - Mechanical control through graphite samples (tensile strength)
 - Graphite properties control : density with and without impregnation
- Tubes : Resistivity and Flexural strength

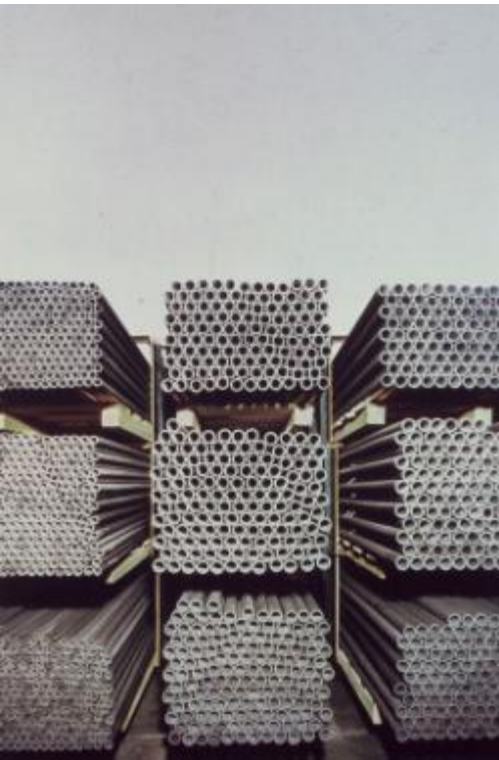
Graphilor® 3 for blocks and columns

	BS	Graphilor® 3		
		XBS	XC	XTH
				
Graphite	S – Fine grain	X – Ultra-fine grain		
Resin	Phenolic	Phenolic	Carbon	PTFE
Parts Available	All diameters	All diameters \leq 900 mm	$<$ 900 mm	\leq 600 mm
Temperature	200 °C	220 °C	430 °C	230 °C
Mechanical strength TUV Homologation	G 18-15-200	G 20-00-220	G 18-00-430	G 15-00-230

Graphilor® 3 for tubes



- Tubes are made with Graphilor® 3 XBS
 - Graphite grade X – ultra-fine grain
 - Resin Phenolic
- Temperature : 220°C
- High Mechanical strength : All our tubes are homologated G30-00-220 which is the highest available in the market
- Manufacturing process only available in France



TUV Homologation

T
H
E
O
R
Y

Nature of the materials

Minimum tensile strength in Mpa (N/mm²) at ambient temperature

Variation in % tensile strength per 100°C, between the ambient temperature and the temperature indicated by the third 3-figure number.

Maximum operating temperature in continuous service (temperature of the material).

G 30 - 00 - 220

E
X
A
M
P
L
E

G is for Graphite

TS = 30 Mpa at 20°C

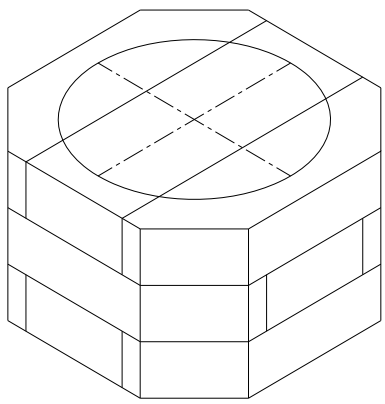
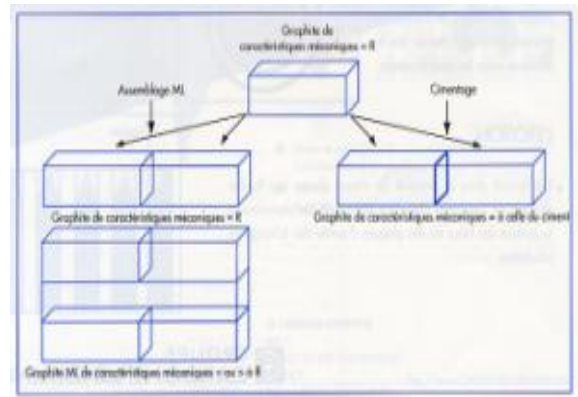
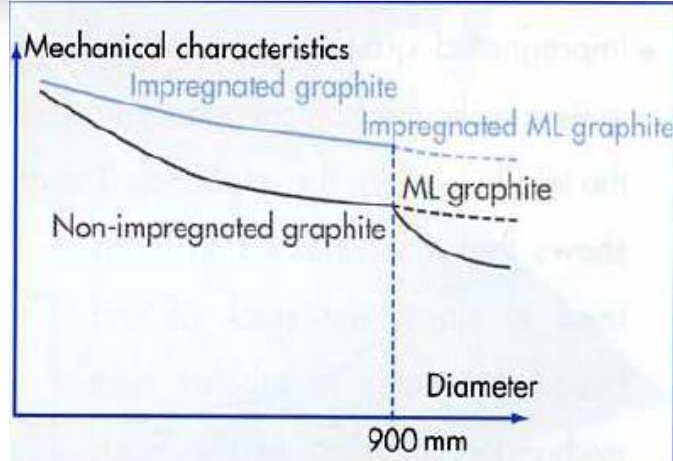
0% variation per 100°C between 20°C and 220°C

Maximum temperature resistance 220°C

Option - Graphilor® ML

Graphilor® ML suitable for large diameters up to 82"

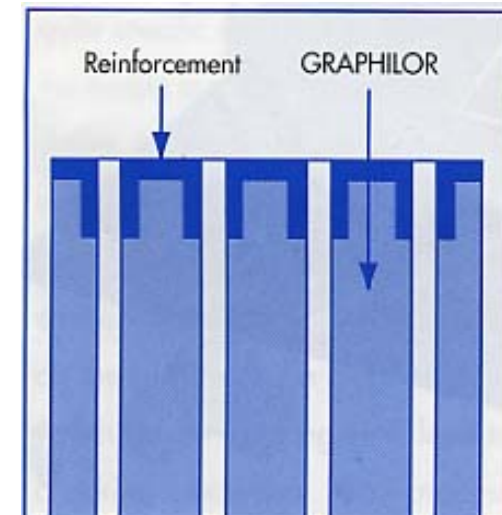
- High mechanical resistance
 - much better than monolithic graphite in large diameter
 - similar to small diameter properties
- Low resin content => no cementing



Option – Rigilor®

Rigilor® is used for large blocks and tubesheets
Main feature : abrasion resistance x 6

- Strengthening of graphite parts by means of a carbon fiber based layer
- Impregnation after applying the Rigilor® coating provides excellent homogeneity of the material with the same properties as graphite
- Mechanical resistance x 2
- Phosphoric acid evaporator : Tubesheets are reinforced by Rigilor® fibers and amorphous carbon sleeves to increase the lifetime.



- CL developed wrapped tubes to enlarge its portfolio
- External brushing before wrapping to improve adherence of fibre
- Pre-impregnation of the carbon fibre phenolic resin (same used for tubes impregnation)
- Automatic polymerization by catalyst
- Tubes are available up to 6 meters without a join



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Applications

- Graphilor[®] 3 XBS : suitable for 80% of applications
 - Available up to 220°C
 - Excellent corrosion resistance (refer to the enclosed corrosion chart)
- Graphilor[®] 3 XC : suitable for very high temperature up to 430°C
 - Top blocks and furnace of Sintaclor[®] (HCl Synthesis Unit)
 - Quench of hot gas and Gas cooler Polybloc[®]
- Graphilor[®] 3 XTH with high corrosion resistance properties
 - Approved material for HF / HNO₃ pickling bath
 - Solvent condenser for multi-purpose batch reactors in fine chemical / pharmaceutical plants