R&D
Carbon

PILOT EVALUATION OF GREEN NEEDLE COKE FOR GRAPHITE ELECTRODES

PREPARATION AND TEST METHODS

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1 Introduction

Needle cokes used for graphite electrodes can be manufactured out of petroleum refinery decant oil or from treated coal tar soft pitch that beside their aromaticity are low in Sulfur and Nitrogen. The selection of specific coking conditions (high pressure and recycling, but also optimum temperature for lowest viscosity level) favorable for the production of acicular (needle like) coke from mesophase in the liquid residuum is the key for high quality needle coke.

The calcination at high temperature of such high quality coke allows the production of the so-called super premium (SP) needle coke used today as raw material for the manufacture of Ultra High Power (UHP) electrodes that can be graphitized rapidly in modern Length Wise Graphitization (LWG) furnaces. However any sub-optimum feedstock characteristics and/or coke production step leads either to scrap issues in LWG furnace or limits the usage of such coke for the production of the largest diameter electrode that reaches today 800 mm. In extreme cases the coke electrode can only be graphitized in slow-heating rate ACHESON furnaces, which represents a serious drawback for modern plants. Down-graded cokes are sold as Normal Premium (NP) or even as Intermediate coke while a conventional low S coke without needle like structure (anode-grade basically). This material is sold as electrode coke for small diameter electrode used in Regular Power (RP) furnace.

The cokes for graphite application are purchased with a substantial price differential reaching 20 % to 40 % for needle cokes, while electrode coke is sold to about one third of the price of super premium material. Frequently the CTE of the coke is given as the key property, decisive for its price level, and in some cases its puffing behavior is ranked in second position. This property is measured on small baked 19 mm extruded artifacts, made out of a blend of fines and a constant pitch percentage, heated in a push-rod or optical viewer dilatometer without longitudinal pressure. The CTE is often reported in the range of temperature from 20°C to 100°C, where the relative difference of the coke grades is high. That is far away from the temperature range of the industrial application where the CTE relative differences are much smaller. The puffing is often measured with rapid heat-up rate reaching 1500°C/h in order to enhance once again behavior differences.

Usually the pitching requirement aspect related to porosity differences is not addressed and the relevant property of laboratory extruded artifacts made with fines are not tested nor reported.

All these testing peculiarities and limitations have been taken into consideration for developing a pilot plant procedure which is as close as possible from modern industrial conditions, procedure presented below.

Emphasis has been given to large extruded artifacts diameter allowing large maximum size of grains and to the graphitization under a typical pressure and with a heat-up rate prevailing in the LWG production furnaces (500°C/h). To validate this pilot plant tool, 10 Premium (5 Super, 5 Normal) cokes and one electrode grade coke have been selected and tested in the RDC pilot scale and research laboratory.

2 Raw Materials

2.1 Green Needle Coke Testing

The “as received” 150 kg of green needle coke will be divided in order to produce a representative 5 kg sample which will be tested in the R&D Carbon laboratory. The properties shown in the table below will be performed.

Pos	Properties	Unit	Method
1	Water Content	%	ISO 11412
2	Volatile Matter	%	ISO 9406
3	Hardgrove Grindability Index	-	ISO 5074
4	Sieving Analysis	%	ISO 12984
5	Elements XRF	%, ppm	ISO 12980
6	Ash Content	%	ISO 8005

Figure 1: Properties of Green Needle Coke

2.2 Pilot Calcining of Green Coke

The sample of green needle coke will be calcined at R&D Carbon laboratory in two steps. Firstly, the volatiles present in the green coke will be removed in a pilot rotary kiln at a temperature of 750°C (load rate of 20 kg/h).

In a second step, the coke will be calcined in a static pilot furnace in order to reach a final real density of about 2.14 kg/dm^3.

The following calcination program will be applied:

RT – 200°C	: 200°C/h	800-1’350°C	: 50°C/h
200-800°C	: 100°C/h	1’350°C	: Soaking time of 5h

Figure 2: Pilot Rotary Calciner

2.3 Calcined Needle Coke Testing

The sample of calcined needle coke will be divided to produce a representative 5 kg sample which will be tested in the R&D Carbon laboratory. The properties shown in the table below will be performed.

Pos.	Properties	Unit	Method
1	Water Content	%	ISO 11412
2	Oil Content	%	ISO 6997
3	Sieving Analysis	%	ISO 12984
4	Tapped Bulk Density	kg/dm3	ISO 10236
5	Grain Stability	%	ISO 10142
6	Pulverizing Factor	-	M168
7	Real Density Xylene	kg/dm3	ISO 8004
8	Crystallite Size Lc	Å	ISO 20203
9	Interlayer Spacing C/2	Å	ISO 20203
10	Specific Electrical Resistance	µΩm	ISO 10143
11	N Content	%	ASTM D5291-02
12	Elements XRF	%, ppm	ISO 12980
13	Ash Content	%	ISO 8005
14	Pore Distribution Hg 2000 bar	-	DIN 66133
15	Resiliency 500 bar	%	M200
16	Pore Axial Ratio	%	M109-1

Figure 3: Properties of Calcined Needle Coke

3 Paste Production

A minimum quantity of 100 kg of coke is needed for the production of 10 extruded rods of 200 mm length (diameter 85 mm) for three different pitch content levels on longitudinal and transversal cores. In total 30 rods representing about 80 kg of paste are extruded.

The dry aggregate is prepared by using a battery of crushers, a continuous sieving machine and an air collision mill with air classifier for the production of fines.

Figure 4: Pilot plant dry aggregate preparation

The following formulation (straight line approach for grains) has been applied:

8-4 mm	:	14 %	1-0.5 mm	:	14 %
4-2 mm	:	14 %	0.5-0.25 mm	:	14 %
2-1 mm	:	14 %	3500 Blaine Fines	:	30 %

The 3500 Blaine fines obtained by adapting the classifier according to the measured fineness during the production were additionally tested with laser granulometry to meet a $d_{50\%}$ size of 50±2 µm or a level in the range of 70±3% for the material passing the 200 Mesh sieve.

A 1% iron oxide inhibitor (<100 µm particle size) addition level was chosen.

A recipe of 5.5 kg of dry aggregate was preheated at 200°C and placed in a heated intensive impeller mixer and mixed with the corresponding percentage (reported relatively to the coke weight like in the graphite electrode industry, and not to the total paste weight) of crushed cold coal tar pitch having a 112°C Mettler SP and 8% QI.

Figure 5 : Intensive impeller mixer for high density paste (10 l)

The final paste temperature after 10 min. mixing was kept 60°C above the softening point of the pitch, i.e. at 172°C, which is typical in the electrode industry. Five batches at each pitching level are prepared successively and shaped at a low density level in a forming machine (RDC 202 pilot vibrator at 20 bars hydrostatic pressure) having a 215 mm diameter mould heated at 150°C.

The first 5 batches are prepared with 24 % pitch to minimize the risk of press clogging due to high pitch requirement of a given porous coke. The other two pitching levels are selected according to the extrusion pressure observation and to the green apparent density of the extruded rods.

4 Extrusion of the Rods

The five semi-shaped electrodes showing a low density level around 1.5 kg/dm^3 are kept in an air drying oven at 130°C and eventually transferred into the extrusion press. An extrusion temperature of 125°C in average is obtained as the press has an oil circulation maintaining the mud material to this temperature level.

The extrusion press has a plunger cylinder of 500 mm diameter driven by oil reaching a maximum hydraulic pressure of 200 bars corresponding to a 400 tons load. The pilot extrusion press has a cylindrical mud of 218 mm with a die of 85 mm. i.e. a reduction ratio of about 2.5.

The extrusion speed is set manually to a constant 100 mm/min. The first meter of the rod is discarded; the temperature of the extruded rods and the hydraulic pressure are monitored. 3 rods with a length of 85 cm for each pitching level are collected on a cart having multiple semi-tube elements where they are cooling down to ambient temperature.

Figure 6: 400 tons extrusion press for 85 mm green rods

After cooling down, the rods are cut with a precision wheel saw to 200 mm length cylinders. These are weighed and their dimensions are measured for density calculation.

It was observed that for conventional porosity needle cokes the pitching is close to optimum when the hydraulic load reaches a level close to 180 tons (hydraulic pressure of 90 bars). The next two pitching levels have therefore to be chosen ideally to get pressure levels above and below this threshold.

5 Baking of Rods

The baking is made in an electrical baking furnace where 4 rods are packed into a 10 liters steel container with granular packing coke. The heat-up rates are as follows:

20°C to 200°C	:	200°C/h	700°C to 1100°C	:	50°C/h
200°C to 400°C	:	10°C/h	1100°C Soaking time of 20h		
400°C to 700°C	:	30°C/h			

After baking the rods are weighed before and after cleaning of the packing material for to determine the sticking propensity. This is a good indicator of the paste pitching status. After the determination of the baking loss, 6 of the 10 rods are longitudinally core drilled to 50 mm diameter and are cut to 130 mm length for the determination of the baked density, which is used for the calculation of the baking shrinkage. 4 cores of 40 mm are also prepared from the same rods. These last short cylinders are used as end spacer for the two runs of longitudinal graphitization along with the six (2 x 3) 130 mm cores.

The 4 remaining rods are core drilled transversally in order to obtain 7 transversal cores of 60 mm length for the graphitization and 2 end spacers of 25 mm length.

Figure 7: RDC 167 Pilot Baking Furnace BF24

6 Graphitization

Only the cores from the recipe which showed the optimum pitch content will be graphitized. The optimum pitch content will be determined from the baked properties as well as from the extrusion parameters. The graphitization process is described in the next pages.

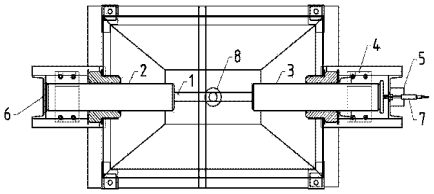
6.1 LWG Pilot Furnace

An 80 kW electrical furnace was designed and built for graphitizing, under mechanical load, baked specimen of 50 mm diameter.

Figure 8: 80KW LWG Pilot Scale Furnace

A rectifier with 4'000 A nominal current and voltage not exceeding 20 V was used as a DC current power supply for heating a cylindrical sample up to 3'000°C. A temperature controller and a data acquisition system with a graphic display were installed. This ensured a fully automated operation and data treatment. The expansion, the post baking shrinkage tendency, the puffing in the intermediate temperature range and eventually the high temperature contraction related to the graphitization process can be monitored under well controlled heat-treatment conditions.

The electrode material to be graphitized can have a length up to 500 mm. It is clamped in between two graphite electrodes of 150 mm diameter that are connected to the rectifier unit (see figure 11). The pneumatic pushing device can provide an effective max. load of 250 kg onto the carbon material which corresponds to a specific pressure of 1.25 MPa. This level is exceeding the one observed in full size LWG furnace. A standard 150 kg load corresponding to 0.75 MPa was chosen.



1. Sample ⌀50mm, l = 470mm
2. Fixed graphite rod ⌀150mm
3. Movable graphite rod ⌀150mm
4. Electrical clamp device
5. Pneumatic pusher device
6. Fixed and el. insulated end
7. Length transducer
8. Pyrometer unit

Figure 9: Sketch of the Pilot Scale Furnace Unit

One graphite electrode is pressed onto a fixed frame end while the other moves following the dimensional changes of the carbon sample during the heating and cooling phases. Both ends of the frame-side are maintained under mechanical tension to minimize external deformations. The gross dimensional changes are monitored by a length transducer probe having a 10 mm range with a resolution of 1 µm.

The sample surface temperature is measured by a pyrometer installed in the center of the carbon column to be graphitized. The pyrometer camera is mounted on a graphite tube, where a sapphire disc is inserted for preventing any gas attack damage to the sensor unit. The bottom of the tube is purged with Argon in order to avoid measurement bias due to fumes evolving from the heat-treatment zone. The emissivity factor is set to a constant level of 0.70 over the entire temperature range. The pyrometer reading starts at a temperature around 650°C.

The electrical clamp connections to the graphite electrodes are simply cooled by natural air convection. The oxidation of the specimen and of the graphite electrodes is minimized by the presence of a thick (0.5 m) layer of packing coke (< 4 mm sizing) which can be loaded and unloaded easily to and from the graphitizing vessel using an emptying screw device and a transfer bin.

6.2 Graphitizing Run and Monitoring of Data

At the beginning the electrical power is applied with a linear current increase of 600 A/h until the pyrometer signal is detected. Then the current is adapted for a constant linear temperature increase of 500°C/h. The gross length change, the applied current (I) and resulting voltage (V) are recorded along with the sample surface temperature. The calculated specific electrical resistance (SER) is derived from the total resistance (R=V/I), taking into consideration the initial cross-section and measured length of the given sample.

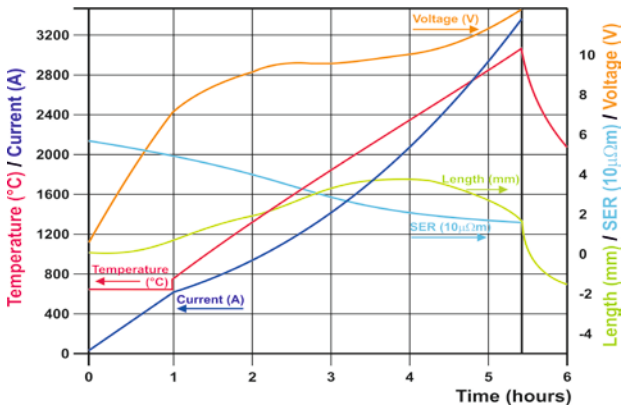


Figure 10: Graphitization test curves

The gross length change of the sample is corrected by the deformation previously observed in a blank test where a graphite standard rod having known CTE over the temperature range was heated in the same conditions.

A detailed study was performed for the selection of the graphitizing conditions in this pilot LWG furnace. For this purpose homogenous samples taken in pilot extruded baked electrodes were used. A regular coke and a 110°C Mettler softening point pitch were taken as raw materials.

The impact of the specific pressure on the dilatometric behavior is quite significant as shown in the two needle coke electrode examples below, while the influence of the heat-up rate was negligible in the range of 500°C/h to 1000°C/h.

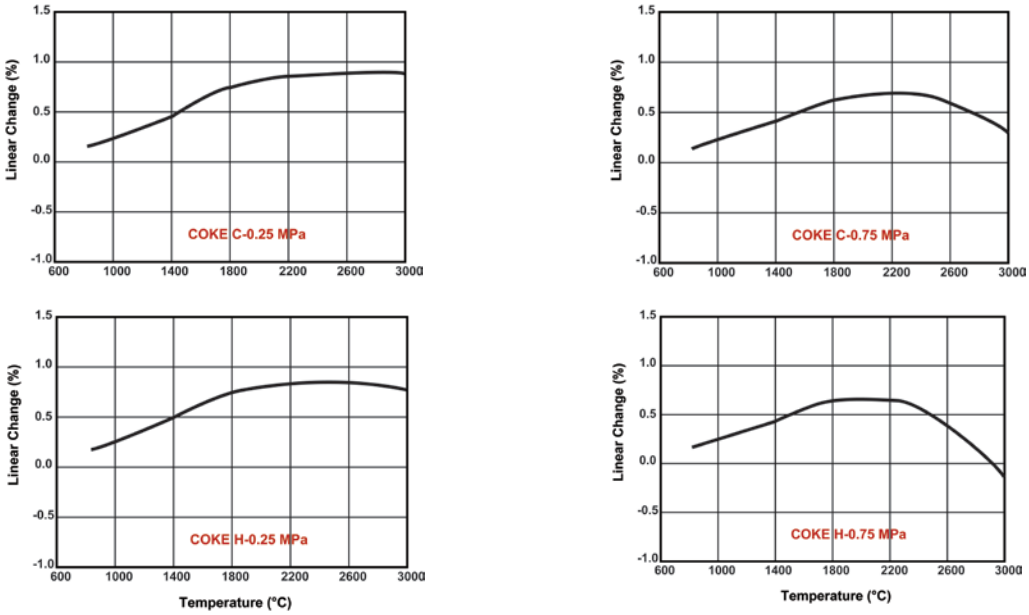


Figure 11: Effect of the pressure on needle coke artifacts during graphitization

A pressure of 0.75 MPa was selected for the pilot graphitization, a level that is corresponding to the industrial conditions.

The repeatability of the net length change is excellent as shown in the figure 12. The band of the testing results is about 0.3 ‰ which is less than 5 % of the typical maximum length change observed at around 2200°C for a typical electrode extruded and baked (10°C/h) at the pilot plant from a super premium needle coke material (8 ‰ in longitudinal direction).

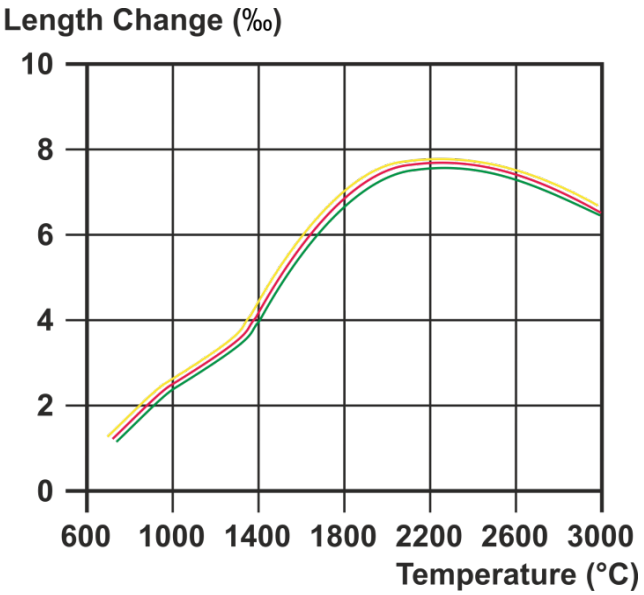


Figure 12: Repeatability of dilatometric curves

Stacked samples gave the same dilatometric curve results as a single core, as illustrated in the figure below. For longitudinal cores, 3 specimen of 130 mm length are stacked with two end-spacers of 40 mm from the same material while for transversal cores a combination of 7 specimens of 60 mm together with 2 end-spacers of 30 mm was chosen.

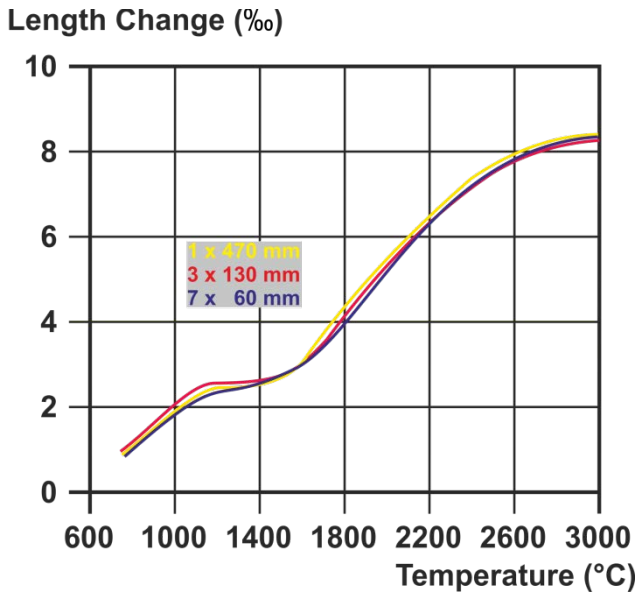


Figure 13: Dilatometric curves for stacked multi samples (130 mm or 60 mm)

6.3 Dilatometric Data

The figure below shows the information that can be gained from the curves.

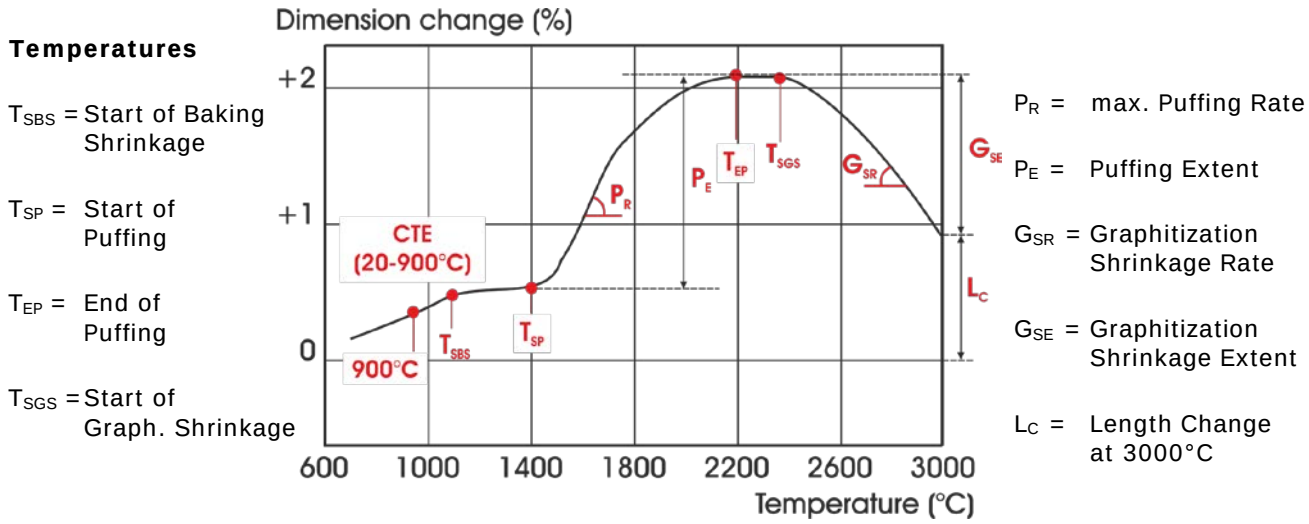


Figure 14: Dilatometric data treatment

7 Laboratory Testing of Cores

7.1 Green Electrode Rods

The following properties will be measured on the 30 green rods (or during the extrusion process):

Pos	Properties	Unit	Method
1	Extrusion Pressure	bar	-
2	Extrusion Temperature	°C	-
3	Green Apparent Density	kg/dm3	ISO 12985-1

Figure 15: Properties of Green Electrode Rods

7.2 Baked Electrode Cores

The following properties will be measured on the 30 (3 x 10) baked rods:

Pos	Properties	Unit	Method
1	Baking Loss	%	-
2	Sticking	%	-
3	Baking Shrinkage	%	-
4	Specific Electrical Resistance	µΩm	ISO 11713
5	Dynamic Elasticity Modulus	GPa	ISO 18142

Figure 16: Properties of Baked Electrode Rods

7.2.1 Longitudinal Direction

From the 30 baked rods, 18 (6 x 3) rods will be longitudinally core drilled and cut to 130 mm. The following properties will be measured on these cores:

Pos	Properties	Unit	Method
1	Baked Apparent Density	kg/dm3	ISO 12985-1
2	Specific Electrical Resistance	µΩm	ISO 11713
3	Dynamic Elasticity Modulus	GPa	ISO 18142

Figure 17: Properties of Longitudinal Baked Electrode Cores

7.2.2 Transversal Direction

From the 30 baked rods, 12 (4 x 3) rods will be transversally core drilled in order to obtain 21 (7 x 3) cores having 60 mm length. The following properties will be measured on these cores:

Pos	Properties	Unit	Method
1	Baked Apparent Density	kg/dm3	ISO 12985-1
2	Specific Electrical Resistance	µΩm	ISO 11713

Figure 18: Properties of Transversal Baked Electrode Cores

7.3 Graphitized Electrode Cores

7.3.1 Longitudinal Direction

The 6 (2 x 3) graphitized longitudinal cores will be measured according to the following testing schedule:

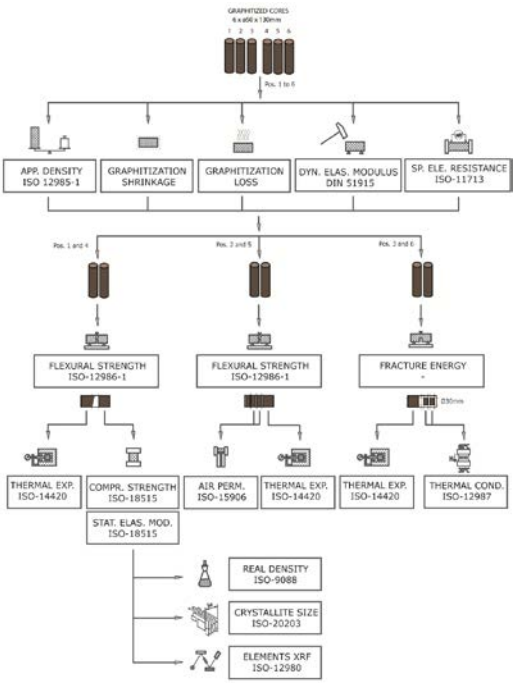


Figure 19: Test Schedule for Graphitized Longitudinal Electrode Cores

7.3.2 Transversal Direction

The 7 graphitized transversal cores will be measured according to the following testing schedule:

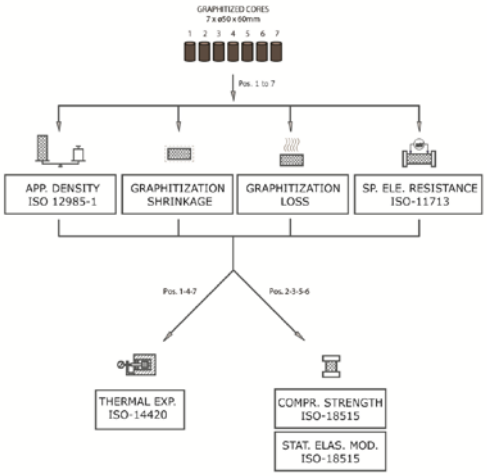


Figure 20: Test Schedule for Graphitized Transversal Electrode Cores

8 Typical Values

8.1 Calcined Needle Coke

Coke Properties		Unit	Typical Ranges of Premium Needle Coke	
			Petroleum Coke	Pitch Coke
Sulfur		%	0.10 to 0.30	0.20 to 0.30
Nitrogen		%	0.10 to 0.30	0.40 to 0.60
Sizing	> 16 mm	%	1 to 10	1 to 5
	> 4 mm	%	30 to 40	30 to 40
	< 0.5 mm	%	12 to 25	10 to 20
Pulverizing Factor		-	1.10 to 1.40	1.10 to 1.50
Grain Stability		%	75 to 90	80 to 90
Tapped Bulk Density	8-4 mm	kg/dm^3	0.73 to 0.79	0.74 to 0.78
	2-1 mm	kg/dm^3	0.91 to 0.97	0.90 to 0.97
App. Density in Hg	100 µm	kg/dm^3	1.74 to 1.78	1.70 to 1.76
Total Porosity		%	16.0 to 19.0	18.0 to 22.0
Sp.El. Resistance		µΩm	430 to 480	430 to 470
Density in Xylene		kg/dm^3	2.130 to 2.150	2.130 to 2.150
Crystallite Size Lc		Å	39 to 45	40 to 48
Pore Axial Ratio		-	0.20 to 0.23	0.21 to 0.24

Figure 21: Typical Values for Calcined Premium Needle Coke

8.2 Green and Baked Rods and Cores

Green and Baked Electrode Properties	Unit	Typical Ranges at Optimum Pitch Content	
		Petroleum Coke	Pitch Coke
Pitch Content	%	22.5 to 24.0	24 to 25
Extrusion Pressure	bar	70 to 100	50 to 80
Green Apparent Density	kg/dm^3	1.72 to 1.75	1.66 to 1.68
Baking Loss	%	6.0 to 6.4	6.3 to 6.6
Baking Shrinkage	%	0.0 to 2.0	1.0 to 3.0
Sticking of Packing Material	%	1.0 to 2.0	0.5 to 1.5
Baked Apparent Density	kg/dm^3	1.63 to 1.66	1.60 to 1.63
Sp.El. Resistance	µΩm	37 to 40	40 to 42
E-Modulus Dynamic	GPa	12.0 to 14.0	10.0 to 12.0

Figure 22: Typical Values for Green and Baked Rods and Cores

8.3 Graphitization Behaviour

Graphitization Behaviour	Unit	Typical Ranges at Optimum Pitch Content			
		Petroleum Coke		Pitch Coke	
		Longitudinal	Transversal	Longitudinal	Transversal
Start of Puffing	°C	1'300 to 1'400	1'450 to 1'550	1'250 to 1'400	1'400 to 1'500
End of Puffing	°C	2'000 to 2'150	2'000 to 2'100	1'850 to 1'950	1'850 to 2'000
Puffing Rate	$10^{-6}K^{-1}$	5.0 to 7.0	0.0 to 5.0	6.0 to 8.0	5.0 to 10.0
Puffing Extent	%	0.20 to 0.30	0.00 to 0.20	0.20 to 0.30	0.15 to 0.40
Start of Graph. Shrinkage	°C	2'250 to 2'350	2'000 to 2'300	2'050 to 2'300	2'000 to 2'200
Graph. Shrinkage Extent	%	0.30 to 0.50	0.40 to 1.00	0.60 to 0.90	1.00 to 1.50
Length Change at 3'000°C	%	0.10 to 0.40	-0.50 to 0.30	-0.20 to 0.00	-0.80 to -0.20
Cold Length Change	%	-1.00 to -1.30		-1.50 to -1.80	
Cold Diameter Change	%	0.40 to 0.80		0.40 to 1.10	
Cold Volumetric Change	%	-0.50 to 1.30		-1.00 to 0.80	
Graphitization Loss	%	2.80 to 3.10		3.20 to 3.60	

Figure 23: Typical Graphitization Behaviour

8.4 Graphitized Cores

Graph. Electrode Properties	Unit	Typical Ranges at Optimum Pitch Content	
		Petroleum Coke	Pitch Coke
Graph. App. Density	kg/dm^3	1.55 to 1.61	1.54 to 1.58
Sp. El. Resistance Long.	µΩm	8.5 to 9.5	9.0 to 10.5
Sp. El. Resistance Trans.	µΩm	17.0-19.0	18.0-20.0
Thermal Conductivity	W/mK	130 to 160	120 to 150
Density in Xylene	kg/dm^3	2.230 to 2.250	2.230 to 2.250
Interlayer Spacing C/2	Å	3.360 to 3.364	3.360 to 3.364
Flexural Strength	MPa	7.0 to 8.0	5.5 to 7.0
Fracture Energy	J/m^2	250 to 320	230 to 300
Compressive Strength	MPa	11.0 to 14.0	10.0 to 13.0
E-Modulus Dynamic	GPa	5.0 to 7.0	4.0 to 6.0
CTE 30-100°C	$10^{-6}K^{-1}$	0.50 to 0.70	0.50 to 0.80
30-300°C	$10^{-6}K^{-1}$	0.90 to 1.10	0.90 to 1.20
100-600°C	$10^{-6}K^{-1}$	1.50 to 1.70	1.50 to 1.80
SER Anisotropy T/L Ratio	-	1.9 to 2.1	1.8 to 2.0

Figure 24: Typical Values for Graphitized Cores