

New materials for the production of graphitised carbon products

Industry urgently needs new sources of carbon products as raw materials to produce graphitised electrodes for EAFs which compete with the same materials required to meet the growing demand for graphitised cathodes for aluminium production. Coal tar based cokes can fulfil the stringent quality requirements for both applications.

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ALUMINIUM smelters are fast moving towards using graphitised cathodes for high amperage pots: the low electrical resistivity of these allow a substantial increase of electric current and so of metal production. This is leading to competition in the demand for graphite electrodes for steel production. In 2008, close to 40Mt of primary aluminium was produced with output growing at around 3.5-4.0% y-o-y excluding China. In China, output in the first half 2010 has grown 44% compared with H1 2009 to around 8Mt compared with 11.8Mt for rest of world. Many Chinese smelters are of modern design and increasingly source graphitised cathodes.

In 2008 a shortage of needle coke to make graphite electrodes occurred as demand for electrodes for electric arc furnaces (EAF) from the steel industry peaked with demand in the order of 800kt in 2009. With the progressive recovery of steel output since 2009, and with the continued growth from the aluminium sector, a return to a shortage can be expected in the near future. Demand, especially from the emergent economies in China, India and Russia, which produce and consume large quantities of graphite electrodes, increasingly require premium needle coke because of its low coefficient of thermal expansion (CTE) as the steel industry increasingly installs ultra-high-power electrical arc furnaces. In 2010, total demand for cathodes for aluminium smelting is estimated at around 250kt, of which 75kt (30%) is for graphitised cathodes.

Western countries and Japan cannot supply much more needle coke from their scarce feed stocks of low sulphur decant oil. Therefore, the development and production of first class coke by delayed coking of coal tar pitch is urgently required to respond to this increased demand.

Delayed Coking Feedstock

For the delayed coking process different combinations of feedstock can be considered such as classical tar, anthracene oil, slurry oil and other residues. The appropriate feeds to the coker require specific pre-treatments. Delayed coking has to be adapted in an optimum way to obtain the correct coke macrostructure which is one ranging from an isotropic to an anisotropic structure depending on the intended application.

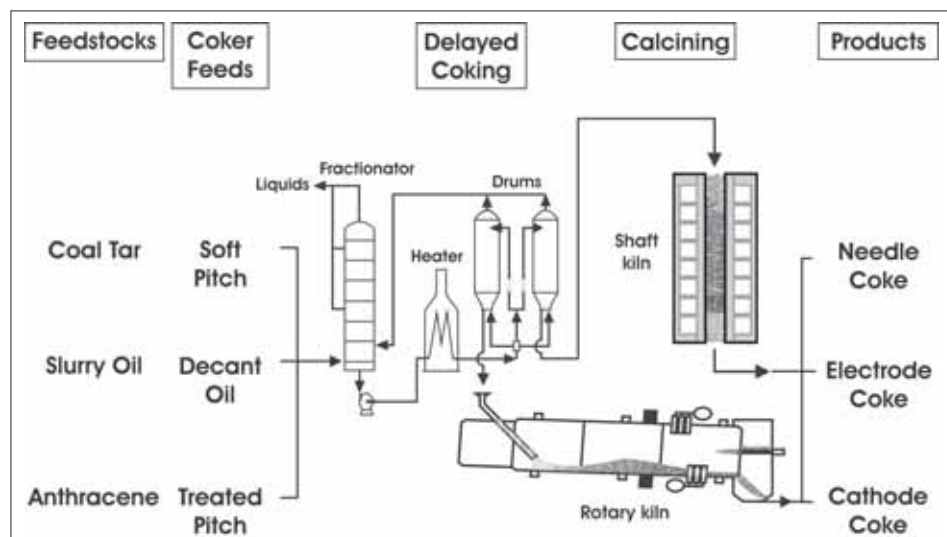


Fig 1 Production of Needle, Electrode and Cathode cokes



Fig 2 Pilot Rotary Kiln at R&D Carbon

R&D Carbon participates in the entire chain of green coke production by providing expertise to companies specialised in delayed coking, such as the US firm, Lummus Technology (Fig 1).

Pilot Green Coke Preparation

The pilot delayed coker facility at the US company, Intertek PARC, was used for the preparation of green coke test samples. The Pittsburgh pilot plant can distill and prepare feed stocks for the later coking step. An 80 litre coker drum processes up to 10 litres of feedstock per hour under optimised conditions to produce needle, electrode or cathode grade green cokes. Typically about 100kg of green coke were produced in duplicate trials.

Pilot Plant for Graphitised Carbon Electrodes

R&D Carbon has invested heavily to up-grade an existing pilot plant built for prebaked anode trials for aluminium smelters to enable it to make graphitised electrode carbon. Now it can also perform detailed evaluations of raw materials for graphitisation. From green coke calcinations to graphitisation of prebaked cores through extrusion pressing, the company is evaluating raw materials for needle and cathode cokes. These evaluations are decisive for the electrode/cathode quality.

R&D Carbon provides the expert interface between coke producers and coke users. In its pilot plant facility in Sierre, Switzerland the following steps can be performed:

- Calcining;
- Dry aggregate preparation;
- Paste preparation;
- Forming by extrusion pressing or by vibrating;
- Baking;
- Graphitising.

Pilot Calcining

The choice both of the calcining technologies and of the corresponding calcining parameters are of paramount importance for the quality of the calcined coke. In R&D Carbon's pilot plant, carbon materials can be either calcined in a rotary kiln (Fig 2) or in a pilot shaft calciner. The plant can reach a throughput of up to 20kg per hour with corresponding heat-treatment and residence time to guarantee the right degree of calcining for each of the different applications.

Preparation of Green Paste & Electrode Artefacts

The dry aggregate is prepared through continuous sieving into fractions and continuous grinding in an air jet mill. Paste is mixed in an intensive impeller mixer. Several batches with differ-

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Property	Unit	Property	Unit
Apparent density	(kg/dm ³)	Coefficient of thermal expansion	(10 ⁻⁶ /K)
Electrical resistivity	(μΩm)	Thermal conductivity	(W/mK)
Flexural strength	(MPa)	Compressive strength	(MPa)
Elasticity modulus	(GPa)	Abrasion rate	(%)
Rapport swelling test	(%)	Sodium vapour resistance	(%)

ent binder contents were prepared for determining the binder requirement (Fig 3).

To shape the carbon product, RDC uses either its pilot vibrocompactor for cathode applications, or its 400t extrusion press to produce 80mm diameter rods. The compacted green samples are baked at 1100°C in an electrically heated pilot baking furnace to remove the pitch volatiles.

Graphitisation

The rods are compressed to 50mm diameter under a pressure of 10 bar, the final step is to graphitise them. Three rods are placed lengthwise in a column and heated in an 80kW pilot furnace for graphitisation. The cores remain under a pressure of 10 bar during the entire process. The length of the sample provides vital information on the puffing behaviour in the temperature range 1200 to 1700°C and on the graphitisation pattern up to 3000°C, as shown in Fig 4.

Testing and Results

After cooling, R&D Carbon thoroughly tests the samples in their research laboratory. The relevant properties are measured for each application, mainly using ISO standards, but also by sophisticated methods including X-ray diffraction, image analysis and microscopy to measure porosity and the macrostructure. The parameters required to make graphite electrodes and graphitised cathodes are listed in Table 1.

Most of the currently available coke materials have already been tested to make graphite electrodes and graphitised cathodes. The results of this standardised evaluation show whether a given candidate material for coke production falls in the 'grey' zone in the graphs in Fig 5 which represents the satisfactory range for each property required for electrode production compared with existing worldwide cokes which have proved satisfactory.

Conclusions

Coal tar-based cokes can fulfil the stringent quality requirements for production of graphitised graphite electrodes for steel production and graphitised aluminium cathodes thereby

Table 1 Parameters measured in samples for graphitised electrodes

Fig 3 Pilot plant to prepare dry aggregate, and 400t extrusion press



filling the impending shortage of conventional materials for these applications. However, the process parameters must first be optimised in careful pilot-scale trials.

With its long experience, know how and infrastructure, R&D Carbon provides the expert interface in the whole chain between technology suppliers, coke producers and coke users so as to:

- Select feedstock and its preparation steps;
- Define process parameters for delayed coking in view of an optimum coke quality;
- Select coke calcining technology and process optimisation;

- Operate pilot plant from green coke to graphite materials;
- Advise on how to use electrode coke for graphite electrodes and cathodes;
- Test and assess quality of coke, electrodes and graphitised cathodes. ■

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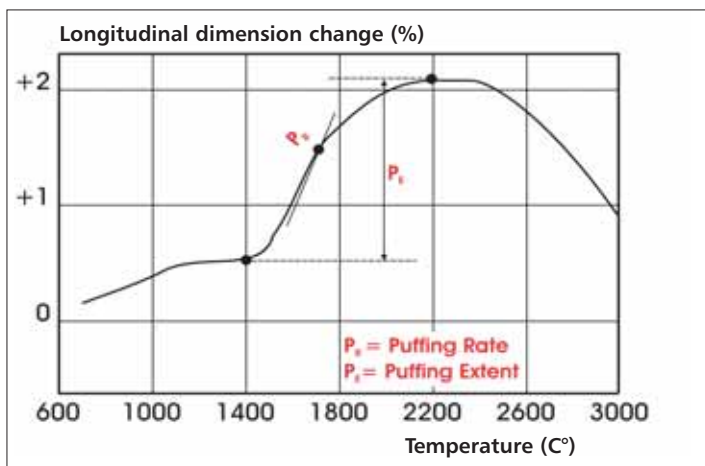


Fig 4 Dilatometry curve during graphitisation

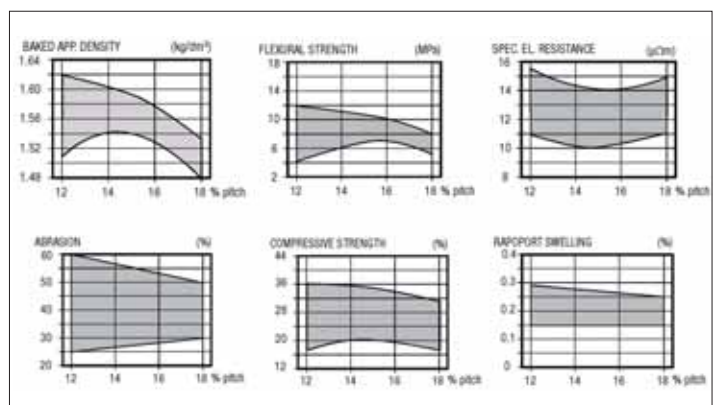


Fig 5 Properties required for graphitised cathodes: the grey zones represent the range of properties known to be in use around the world