Petroleum coke shaft calcining technology - salient features of construction and production techniques

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Abstract:

Calcined Petroleum Coke (CPC) is a vital component in aluminium smelting with a minimum consumption equivalent to one third of the weight of primary metal produced. The traditional specifications and quality limits for CPC in anode production for smelters are becoming less strict in the tightening market. Trends in petroleum crude refining have also deteriorated the quality of Green Petroleum Coke (GPC). In addition to the quality of GPC, the anode grade CPC quality is also determined by the calcination process. Different calcination technologies have distinct cost and quality implications. In China, calcination of GPC is primarily carried out in shafts, while the west and most of the rest of the world mainly uses rotary kiln technology. There are known instances of projects to build calcination shafts outside China, but most have eventually been shelved or cancelled. This article presents facets of Chinese shaft technology construction, operation, maintenance routines and produced CPC characteristics in comparison with rotary kiln technology.

Keywords: Calcined petroleum coke; shaft calcining technology, rotary kiln technology.

1. General

GPC is a by-product of the oil refining process. Heavy Crude Oil (bottoms) are put into a "Delayed Coking Unit" – DCU, Coker – in order to extract further lighter fractions (jet fuel, gasoline, kerosene). The solid carbon mass that remains in the DCU is GPC.

While GPC with high Sulphur levels or shot content is mostly used as a fuel for power or cement plants, sponge-type GPC with lower Sulphur and acceptable metals content commands a higher price and is mostly calcined.

A percentage of between 70 - 80 % of global CPC produced is consumed by the primary aluminium industry as the major component for anodes in the smelting process. CPC is chosen for use both because of its high purity of Carbon and high electrical conductivity.

Traditional and typical specifications and limits for CPC used in anode production are becoming difficult to maintain under a tightening market and deteriorating quality trends of GPC.

2. Calcination

Calcination is a high temperature pyrolysis treatment of GPC that upgrades it to properties better suited for specific industrial end-uses. Calcination implies the heating of GPC in a unit with controlled ingress of air, to safeguard against excessive combustion and burning of the carbon.

The process removes Moisture and Volatile Carbonaceous Matter (VCM or VM) from the GPC, and the amorphous form of carbon transforms partially into a crystalline structure under the elevated temperature over a period of time. The orientation change in the molecules leads to improved crystallite size (Lc) accompanied by improvements in the Real Density and conductivity of the CPC.

2.1. Rotary kiln technology

Uses a rotating horizontal cylinder of steel lined with refractory bricks of high alumina content on the inside. The diameter of rotary kilns is typically between 2.5 to 4.5 meters and their lengths vary from 40 to 80 meters.

The kiln shell is supported on 2 to 3 tyres, which ride on two supporting rollers. The kiln rotating speed; revolution per minute (rpm) is adjusted by means of a Variable Frequency Drive in the range of 0.3 and 2 rpm.

GPC is sized to less than 100 mm lumps, and two or more types stored in silos can be blended prior to introduction into the rotary kiln for calcining.

The schematic of the kiln is shown in Figure 1 and the calcining flow chart in Figure 2. The rotation and the slope (generally about 4 %) of the kiln facilitate the movement of the GPC from the feed end to the CPC discharge end.

An oil or natural gas fired burner at the discharge end is used to preheat the kiln refractory prior to start-up and later to maintain the kiln temperature.

Tertiary air is injected into the kiln via blowers mounted on the kiln shell, and through nozzles to provide air for combustion of the VM released by the GPC.

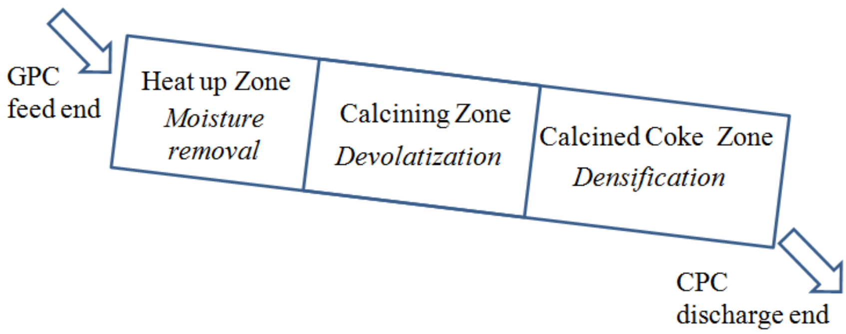

Figure 1. Calcination progress zones.

The heat transfer inside the kiln occurs mainly through radiation from hot kiln gases and the exposed heated surface of the refractory. Heat transfer also takes place through convection from the hot flue gases and some heating also takes place by conduction from the refractory.

As the coke progresses down through the kiln, it moves counter current to the hot combustion gases released by the fuel being burnt at the discharge end and from the combustion of VM emanating from the GPC.

In the initial section of the kiln the GPC loses its moisture at about 200 ºC. De-volatilization occurs in the next section, at temperatures ranging from 600 °C - 1 000 °C. De-hydrogenation, some de-sulphurization and densification of the coke takes place at temperatures between 1 000 ºC - 1 350 ºC in the last section.

Total persons required for maintenance work would be 12, i.e., two teams / groups with 5-6 persons in each team.

7.2. Quality implications, shaft v/s rotary kiln calcination

Sulphur and other chemical constituents of CPC - iron, silicon, nickel, vanadium, sodium and other metals - are consequent to their original level in the GPC(s) used and are not particularly dependent on the calcination process.

The increase in real density and improvement in crystalline structure and electrical conductivity are affected differently by shaft technology.

The low heat-up rate of 1°C/min minimizes porosity caused by VM evolution and leads to improved VBD. There is an absence of the “pop-corn” effect in the higher-volatile matter GPCs, which calcinations can be managed with shaft technology, as against the poor bulk densities which result from such GPCs if calcined in a rotary kiln.

The long resident time of coke with shaft technology enables a higher degree of calcination i.e. higher real density for a correspondingly significant lower calcining temperature than in rotary kilns.

Calcination via shaft technology also enhances CPC particle sizing due to an “agglomeration” effect, the finer coke particles coalescing into coarser grains. Rotary kilns on the other hand undergo degrading of particle sizes due to high heat-up rate vigorous agitation of coke movement in the kiln.