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.

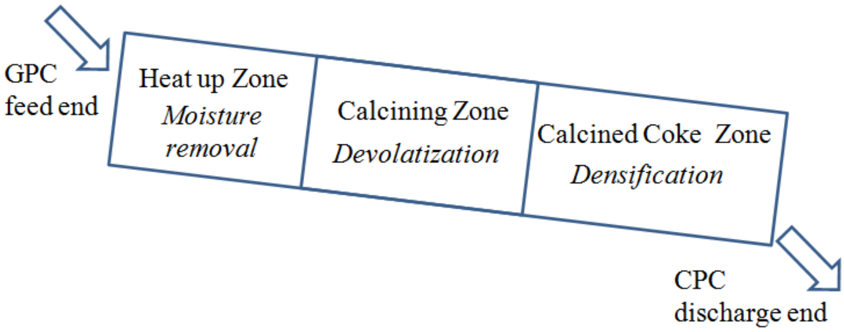

Figure 1. Calcination progress zones.

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.

In the last section, the coke is subject to heat soaking which improves its crystalline structure and physical properties. The CPC next exits the kiln and enters the rotary cooler for the quenching operation.

The dimension of a large Rotary kiln for a typical 350 000 TPA calcination plant is 4.35 m Ø x 78.0 m long with slope at 4.17 %.

The rotary cooler is like the kiln also a cylinder made of steel plate, but smaller in diameter, shorter in length and rotates at a higher rpm. The quenching is done by direct contact of the coke with fine sprays of water. Where water is scarce, or contains significant amount of impurities, indirect cooling is done by circulating water around the CPC with a heat exchanger.

CPC exit temperature is maintained at around 120 ºC, and discharged onto a conveyor belt or a screw conveyor. Mineral oil is sprayed as a de-dusting measure before the CPC is moved to storage.

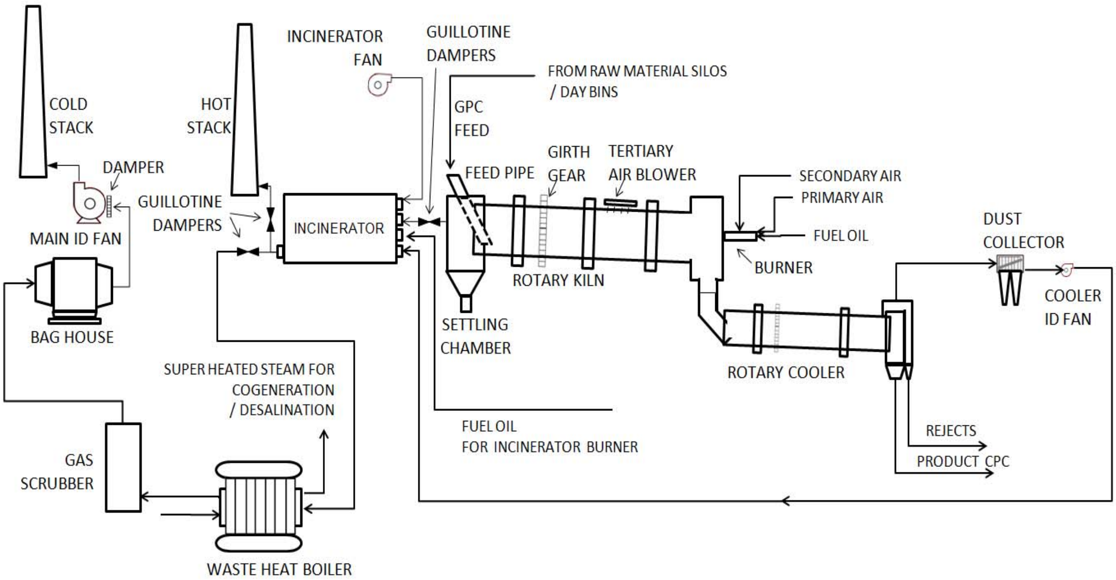

Figure 2. Flow diagram of a rotary kiln calcining plant.

Hot combustion gases, remnant coke fines and Volatile Matter, exit the kiln from the GPC loading end and burn in the Incinerator. The Incinerator is operated under a slight negative pressure, as is also the kiln. Either a stack or an ID fan is used to produce the negative pressure.

2.2. Chinese shaft technology

A shaft calcining unit consists of anywhere between 12 to 56 shafts or pots (Figure 3) to a cluster or "kiln". The inlet hoppers are shown in Figure 4. Chinese calcining plants have multiple clusters and a typical shaft calciner ranges in capacity from 50 000 TPA to 500 000 TPA capacity.

Shaft technology is lower cost in terms of CAPEX and maintenance, provided the VM content in the GPC blend used is under 11 % and excessive fines do not clog the coke descent through the shaft.

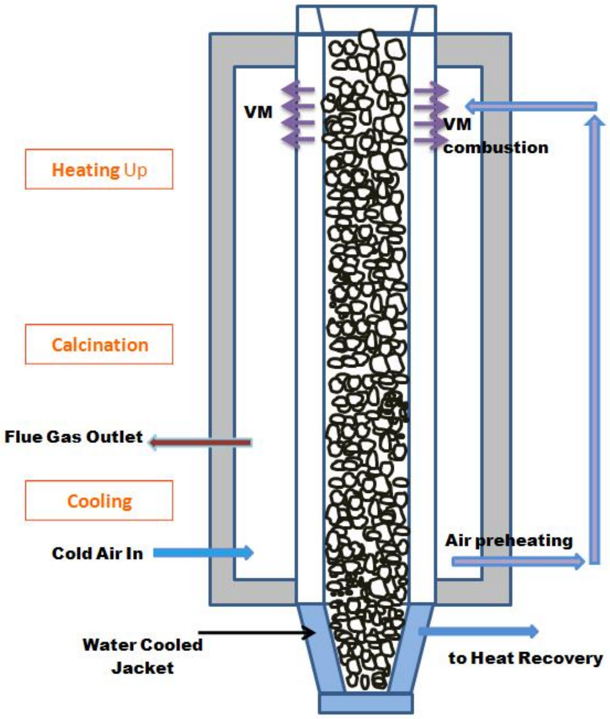

Figure 3. Outline of a typical single vertical shaft,

Figure 4. View of shaft top inlet hoppers.

The slower heat-up rate in shafts results in higher VBD and in lower porosity levels. Both translate into lower costs for anodes produced using shaft-produced CPC, because of lower CTP consumption.

Appropriately crushed and sized GPC is loaded into a hopper at the top of the shaft and moves downwards by gravity. There are no rotating or moving parts in the shaft except the discharge valve. The hot gases moving through flue channels surrounding the shaft heat the GPC. The hot air does not come in direct contact with the GPC mass.

GPC undergoes a similar process of moisture removal, de-volatization and densification during its descent down the shaft as in horizontal rotary kiln calcination.

The evolved volatiles rise through the coke bed and move into the flue wall openings at the top of the shaft, where they are combusted inside the flue gas channels.

The hot gases of the combustion move continuously through the channels enclosing the inner shaft walls containing the column of coke, and provide the heat for calcination, which is transferred to the coke from the flue walls.

Dampers are used to regulate draught and supply of air for combustion at appropriate locations in the flue walls.

The residence time of the GPC in the shaft and heat transfer time for calcining is adjusted by controlling the rate of CPC discharge through the bottom of the shaft.

Modern plants use vibratory conveyors to transport the CPC on to conveyor belts leading to storage.

2.3. Differences between shaft and rotary kiln calcining technologies

GPC is heated indirectly in the vertical shafts as the coke mass moves down slowly. Unlike in rotary kiln calcining, the GPC is not exposed to the flames during the process.

Due to indirect heating and lower air oxidation, the average conversion efficiency of CPC:GPC in a shaft is better than in a rotary kiln and varies from 80 to 82 %.

The lining and refractory laying of the shaft is a highly skilled job and a critical aspect of the technology. Properly designed and calculated expansion slots have to be retained during the lining operation to prevent damage to the refractory during heating-up.

Constant human monitoring of the calcination process is an essential requisite of vertical shaft technology as obstructions in the path of flue gases can lead to damage to the refractory lining and in extreme cases even to explosions.

The heat-up rate in the de-volatilization zone is less than 1 °C/min as compared to over 40 °C/min in rotary kilns. The residence time of coke in a shaft is in excess of 24 hours and can range up to 36 hours, while for a typical rotary kiln, the residence time is about one hours.

Because of the weight load and the compaction in the lower section of a shaft, a degree of agglomeration of the coke grains takes place, improving the grain size of the CPC. However this same trait can also lead to blocking of the coke descent, and is therefore an aspect always taken into account when optimizing the dimensions of the shaft.

3. The interest in Chinese shaft calcining technology

Between 2006 and 2008, availability of traditional quality of calcinable GPCs became extremely tight, and only supplies from previously disdained Chinese shaft calciners enabled the West to meet the increased demand for CPC.

Next, the global economic crisis shut down almost 8 million tons of aluminum production capacity, also changing the fundamentals of the CPC market. Some smelters continued to buy the cheaper Chinese CPCs.

This resulted in CPC producers in the West re-thinking on the economics and quality of the Chinese shaft technology CPC. Investment costs in setting up shaft calciners were lower, almost one third of that for a rotary kiln. The size of CPC produced was better and the Vibrated Bulk Density excellent, leading to savings in pitching for anode plants.

Western calciners and even smelters began giving serious thought to setting up shaft calciners in their countries themselves or having JVs with established CPC producers in China. Rafts of feasibility reports were commissioned. Not everything worked out though. A difficulty was the non-availability of skilled construction and operation technicians outside China. Another was language when workmen were imported from China.

Only two small plants have been built in India with Chinese collaboration, one of which has been re-built twice since it was commissioned in 2008. Two large projects in the Middle East and Latin America did not progress beyond the drawing board. Rain-CII acquired a small shaft calciner in China to understand the technology and replicate it in India. More successful have been JVs in China itself – EGA owns stakes in two calciners in the Jiangsu and Shandong provinces.

4. Facets of Chinese shaft technology

4.1. Shaft construction

Construction is done for complete clusters consisting up to 72 shafts. A typical Chinese shaft project will consist of up to 10 clusters, takes between 6 and 9 months to be completed from the time the foundation is laid and the cluster of shafts is ready for pre-heating.

4.2. Refractory expansion aspects

Refractory is the critical material in the construction of shafts. The high-Silica bricks required have a high Co-efficient of Thermal Expansion (CTE) up to a temperature of 700 °C and flatter thermal expansion at more elevated temperatures (Figure 5).

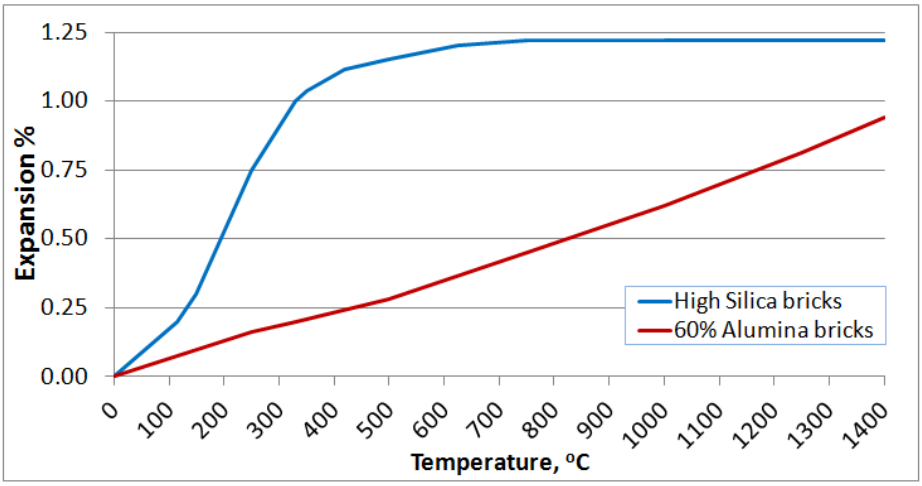

Figure 5. Coefficient of thermal expansion.

This one aspect can be summarized into three cardinal rules for operation and life of shafts:

1. Extreme caution and time of up to 75 days is necessary when pre-heating the shaft. Specific protocols need to be observed for handling the high degree of expansion in joints and springs.
2. Stringent operating temperature range for refractory exposed to temperatures above 750 °C and limits to operating temperature variations.
3. Because of the steep expansion gradient in the range below 700 °C as seen in **Figure 2**Figure 5, cooling cracks the shaft refractory, requiring it to be rebuilt before being restarted. Shafts are operated without lowering temperature below the critical 750 °C level for their entire life.

4.3. Refractory flue paths

Refractory lining of the shaft is critical and has to be done precisely and accurately. This requires professional supervision while laying the refractory bricks, layer by layer. Any blockage in the flue gas path may cause an explosion.

The gaps left and quantity of the refractory mortar used between the bricks are also crucial in the kiln construction. There should be sufficient space provided for expansion during the pre-heating of the kiln.

It is important to use high quality insulation material, to minimize heat loss from the kiln as also to provide safer and comfortable working conditions for the workers. Temperatures can rise very high during the summer season. The atmospheric temperature when the refractory is being installed should not be lower than 5 °C.

4.4. Shaft dimensions and capacity

A typical shaft dimension would be 30 cm x 2 m x 6 m height with a corresponding CPC discharge rate set at about 120 kg/hr. This translates into 2 880 kg output per pot per day and a total of 92 tons per day for a 32-pot cluster. For a calcination plant with 11 shaft clusters the production capacity would be 1 000 tons per day or 30 000 tons per month, assuming no recycling CPC is needed.

4.5. Shaft life

The refractory lining of a shaft once completed, remains till the end of its operating life, which can be around eight years. The shaft life span depends on how well each kiln has been operated and maintained.

4.6. GPC feed considerations

Typically the particle size of GPC feed is maintained smaller than 50 mm, for unimpeded flow down the shaft. Also the proportion of fines in the GPC blend need to be limited, as excess fines reduce permeability for the flow of the volatiles through the shaft and can lead to minor explosions. Fines can agglomerate in the high heat within the kiln, leading to shaft choking. The proportion of fines in the GPC feed is maintained below 30 % to mitigate this impact.

The volatiles content results in condensable hydrocarbons and tars make the coke surface sticky, partly responsible for the agglomeration effect which improves the size of CPC.

The GPC loading hoppers have to contain a minimum level of GPC (about 1/3rd of the height of the hopper) to prevent volatiles from the shaft escaping through the hopper and becoming a flash fire hazard when the volatiles burn after coming in contact with the oxygen in air.

Shaft calcination therefore has a limit to the proportion of VM and fines content that can be used in the GPC. The VM content in GPC used in shaft calcining must be controlled within a maximum limit of 11 %.

4.7. Calcining GPC with high VM and high fines content

GPC containing high VM and high fines content can be calcined with workarounds using Recycled Coke (an option not applicable to rotary kilns because of incremental coke burning on every re-pass through the kiln.)

GPCs having a higher percentage of inherent VM can be calcined, by maintaining the VM content limit in the feed within 9 ± 2 %, by blending appropriate proportions of Recycled CPC. It is not unusual to add between 5 to 15 % of CPC to the GPC blend in shaft calciners.

The overall production rate of the kiln decreases in relation to the percentage of CPC added, but this may be viewed vis-à-vis the cost-benefit equation in making high VM GPC calcinable.

Control of fines content in GPC requires that the natural segregation of particle sizes during GPC handling should not cause excess fines proportion in the GPC feed. The fines proportion control can be maintained by blending in “lumpier” GPC fractions.

The accepted and convenient method in use, to control the proportion of fines too, is to add CPC with suitably low fines content in required proportions, to restrict the content of fines under 1mm below the 30 % limit.

5. Kiln process control and monitoring

5.1. Temperature control

The temperature control of a shaft, the temperature and draught of the flame paths / flue channels, apart from adjusting CPC discharging rate (quantity and frequency), is done mainly by regulating air inflow for combustion through dampers. In some cases air is preheated through a recuperator made of refractory bricks. These air-flow control points are provided at multiple levels along the flame path of the shaft.

Typical material temperature in pots and flame path temperature distribution is shown in the Table 1 below for configuration options with 6 flame paths and 8 flame paths, provided by Zhengzhou Institute of CHINALCO:

Table 1. Kiln temperature levels.

Calcining layer	Kiln with 6 flame paths		Kiln with 8 flame paths	
	Temperature in flame paths (°C)	Material temperature in pots (°C)	Temperature in flame paths (°C)	Material temperature in pots (°C)
1	1000 - 1100	200	1000 - 1100	250
2	1250 - 1350	570	1250 - 1350	700
3		790		920
4		1000		1120
5		1100	1250 - 1350	1270
6	900 - 1000	1040		1290
7				1200
8			900 - 1000	1100

Air flow dampers in Layer 1 and Layer 2, are adjusted for complete combustion of volatiles to maintain kiln temperature. Controls in all 8 layers must be adjusted to maintain negative pressure to prevent VM and flames from breaking out. Temperature of flue gas exiting the kiln before entering the boiler is less than 1 000 ºC

If the volatile content is inadequate the air ingress may need to be reduced and preheated air used instead, so as to ensure suitable temperature for each layer.

5.2. Cooling process

Monitoring of the cooling process involves monitoring the water temperature levels, and the physical status of the water jacket, for instances of water leakage or water flow malfunction. Water temperature entering water jacket is less than 45 ºC. The temperature of water coming out from water jacket should be less than 60 ºC.

5.3. CPC discharge rate

Control of CPC discharge also determines the residence time of the coke in the kiln. The coke residence time is very long in a shaft calciner and could vary from 28 - 36 hours. The temperature of the discharged CPC should not be higher than 200 ºC.

6. Maintenance of shafts

A kiln will typically run for around 8 years without any need for stopping the calcination process for maintenance. There have been instances of shaft operation being reduced because of adverse market conditions and other external reasons. But the shaft cannot be shut down completely.

Regular routine cleaning termed "Small Cleaning" in Chinese terminology is important, and covers the routine maintenance of the air and VM channels, to remove the tarry deposits that build up over time. Discharge has to be paused for about 15 - 20 minutes when air blowing the VM channel, only for the specific shaft under cleaning at the time.

The cleaning cycle periodicity is typically twice a month, which can be fine tuned as per need determined by sulphur content (lower the sulphur, lesser the frequency).

It should be noted that the maintenance personnel deployed for the small cleaning operations need to work in a relatively harsh environment, at elevated temperatures and dusty surrounding.

In abnormal situations when there is a need to remove deposits from the shaft walls, a "Large Cleaning" activity needs to be carried out. The 'oxidation method cleaning', is for cleaning the long time coking deposits on the shaft wall. The location of coking area on the shaft wall is exposed to air and with continued calcination for 1 - 2 hours the coke oxidizes and falls off. Most well operated kilns do not have to do the large cleaning during the life of the kiln.

7. Pros and cons, shaft v/s rotary kiln

Pros

- Vertical shaft calcining improves the grain size of CPC produced due to the agglomeration effect and results in lower porosity and higher VBD
- Refractory costs are lower given the absence of rotation wear and tear
- Carbon losses are lower as coke fines are not entrained in the exhaust gases
- Lower particulate matter and CO_2 (up to 40 %) in the exhaust gases
- Fuel consumption is avoided as shaft calcining is energy self-sufficient
- Large scale incineration / settling chamber is not required, as minimal fines and VM are carried in the shaft exhaust stream
- There is no natural segregation of particles
- All coke particles reach the maximum temperature resulting in uniformly consistent calcination levels
- Specific investment costs are lower and CPC yield better.

Cons

- Controls rely to a large extent on the throughput rate and human intervention, which becomes rather approximate in nature
- The "agglomeration" of fines can block flow of the coke the kiln, if constant monitoring and due care is not exercised at all times

- Manpower requirements are higher and viability of the technology depends upon manpower costs in a given location
- Productivity in terms of plant size and manpower requirements is lower.

7.1. Manpower

Man power requirements for shaft operation are significantly higher than that for a rotary kiln. Manpower deployment for calcination activities and maintenance work force, given below are for a typical set-up consisting of 11 shaft kilns (~ 350 000 tpy CPC) and corresponding capacities upstream and downstream. The total cost for manpower requirements will depend on region specific determination of labour costs.

Manpower for operations

GPC loading – with automated GPC loading operations systems in place, a maximum of 2 persons per shift can monitor multiple shaft kiln clusters in one location.

Kiln Process - One person is required per kiln per shift for temperature control (Figure 6). Hence for 11 shaft kiln clusters, 11 persons will be required as Temperature Controllers per shift, including monitoring draughts and temperature profiles and controlling dampers for air flow for combustion and draughts.

Figure 6. Skilled operators keep the coke moving in the shafts.

CPC discharge – this operation needs up to 2 persons per shift, assuming standard operation mechanisms for the discharge section – mechanized opening for CPC discharge, conveyor for handling of discharged CPC and monitoring of cooling jackets.

Total for the calcination process - For 11 shaft kiln clusters the total workforce for the calcination process would be 15 persons per shift.

Maintenance “Small cleaning” - Two teams of 5 to 6 persons can work in parallel, each on a different shaft. Thus with 2-3 shifts of 8 hour each are needed to complete small cleaning on each kiln. One team will be able to undertake work of 6 kiln shafts in 12 to 18 work shifts (each shift of 8 hours), with the routine repeated every fortnight.

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.