Production and Application of Calcined Coke In Rotary Kilns Calciners  
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Abstract—Calcined coke is the best material for making carbon anodes for smelting of alumina to aluminum. Petroleum coke is usually calcined in a gas-fired rotary kiln or rotary hearth at high temperatures, around 1200 to 1450 °C, to remove moisture, drive off volatile matters, increase the density of the coke, increase physical strength, and electrical conductivity of the material. Rotary kilns have been used successfully for many years to produce calcined coke for the aluminium industry and they offer a high level of automation, performance and flexibility. Shaft calciners make a high bulk density, coarse particle size product and several papers have been published recently highlighting these benefits. This paper presents a comparison of the operation of two different kiln and calcining technologies as a product quality and process performance. Several misconceptions about the technologies related to operability, product quality and their ability to handle a wide range of green coke and calcinations processes. All technologies used in a complimentary manner in the future. Density, Size and Reactivity of coke and Impurity are most effective parameters on calcined coke quality.

Keywords—Calcination, coke, rotary Kiln, petroleum

I. INTRODUCTION

Calcined Petroleum Coke (CPC) is manufactured from Raw Petroleum Coke (RPC) by the process known as high temperature pyrolysis. Several papers have been published over the last 5 years comparing rotary kiln calciners to shaft calciners [1,2,3,4]. Shaft calciners are common in China but there are very few operating outside of China. Rotary kilns on the other side, have been the technology of choice for most of the rest of the world and the technology is generally well known and understood. The industry trend is towards lower real density and several papers have been published on this recently [5, 6].

The process is carried out in a rotary kiln at temperatures exceeding 1300 deg C. Calcination of CPC is essentially a high temperature treatment in which the carbon to hydrogen ratio of RPC is increased from 20 to 1000 and above. Calcination is achieved by complete demoisturisation and dehydrogenation of RPC under controlled conditions. During the process molecular rearrangement takes place making the CPC electrically conductive, an essential property required for Aluminium smelting.

Raw Petroleum Coke needs to be calcined in order to meet the requirements for producing Graphite Electrode used in steel-smelting or Anode Paste used aluminum and magnesium. The calcination temperature will usually be about 1300°C. This is done to get rid of the volatility, which will help to reduce the content of hydrogen and increase the graphitization degree of Petroleum Coke products so as to enhance the strength of high temperature and heat resistance and to improve conductivity of Graphite Electrode. The following table illustrates the difference between fuel grade green coke and coke intended for aluminum anode grade before and after calcining. These two grades (fuel and calcined) are representative of the two extremes of petroleum coke composition.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fuel-Grade Green</th>
<th>Anode-grade Calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur (wt%)</td>
<td>2.5 – 5.5</td>
<td>1.7 – 3.0</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>01 – 03</td>
<td>01 – 03</td>
</tr>
<tr>
<td>Nickel (ppm)</td>
<td>ND</td>
<td>165 – 350</td>
</tr>
<tr>
<td>Vanadium (ppm)</td>
<td>200 – 400</td>
<td>120 – 350</td>
</tr>
<tr>
<td>Residual Hydrocarbon (wt%)</td>
<td>9 – 12</td>
<td>0.25</td>
</tr>
<tr>
<td>Bulk density (g/cm3)</td>
<td>ND</td>
<td>0.80</td>
</tr>
<tr>
<td>Real density (g/cm3)</td>
<td>ND</td>
<td>2.06</td>
</tr>
</tbody>
</table>

A diagram of typical kiln calciner is shown in figure 2. Calcined coke is produced from delayed process green coke by a process of further heating at temperatures up to 1200°C. The product of calcining removes virtually the entire residual hydrocarbon including PAHs and the result is a dustier material. Calcined coke is characterized as either anode-grade coke or graphite needle-grade coke depending upon its physical and chemical characteristics with needle-grade coke having a higher purity than anode-grade coke which is used in electric furnaces in aluminum and steel smelting. Petroleum coke calcining may be achieved in a rotary kiln, shaft calciner and rotary hearth.

A rotary kiln is a device that supplies tremendous amounts of heat in order to change the chemical composition of an object. It is made up of a strong reinforced steel outer shell that is coated with a heat-resistant inner lining, support rollers and a drive gear to keep the contents in a continuous rotating motion and internal heat exchangers capable of producing...
temperatures well over 1500 degrees Celsius. Rotary kilns will sit slightly at an angle so that the inner contents will be sifted downwards toward the heat source and allow for any evaporative gasses to escape from the top during the process through sealed ductwork. The contents are then sorted and ejected through an opening in the lower end of the device that automatically sorts processed materials and waste into separate bins. Other common terms to describe such a device may be a rotary kiln incinerator or a rotary kiln dryer. The kiln is a cylindrical vessel, inclined slightly to the horizontal, which is rotated slowly about its axis. The material to be processed is fed into the upper end of the cylinder. As the kiln rotates, material gradually moves down towards the lower end, and may undergo a certain amount of stirring and mixing. Hot gases pass along the kiln, sometimes in the same direction as the process material, but usually in the opposite direction.

Steel: Pet coke is a partial replacement for metallurgical coal as a feedstock for coke oven batteries, and as a partial substitute for pulverized coal directly injected into blast furnaces. Pet coke that is specially produced to have a needle-like crystal structure is called needle coke. Needle coke is used to produce the electrodes used in steel production. No other material has needle coke’s combination of electrical conductivity and physical properties required for these electrodes. Calcined pet coke is also used as a recarburizer in the steel industry. Recarburizers are used to make minor adjustments to carbon content to ensure that each batch of steel meets specifications for carbon content.

For other uses calcined pet coke is used in lime production. lime is used in many industrial processes including steel production. CPC is gasified to produce ammonia and urea ammonium nitrate, which is then used in fertilizer production, and by pulp and paper mills. If a refinery does not have a coker, then the crude residue is either used to produce asphalt, blended with some valuable lighter products to produce residual fuel oil, or goes through an alternative conversion process. The major use is in the Aluminium industry for the production of pre-baked carbon anodes used in the smelting process. World petroleum coke consumption in 2016 is shown in figure 2.

Fig. 1 Diagram of counter current calciner

II. USE OF CALCINED PETROLEUM COKE

Petroleum coke is used as a source of energy, or as a source of carbon for industrial application. Fuel grade pet coke represents nearly 80 percent of worldwide pet coke production and is a source of fuel for cement kilns and electric power plants. Calcined pet coke (CPC) has the highest carbon purity and is used to manufacture energy, as well as in aluminum, graphite electrode, steel, titanium dioxide and other carbon consuming industries. Aluminum: Worldwide, more than 85 percent of all CPC is used to produce anodes for smelting alumina into aluminum via the Hall-Héroult process, and there is no other commercially viable method to produce primary aluminum (bauxite ore is refined into alumina via the Bayer Process at alumina refineries). Anthracite coal was originally used as the carbon source; however, CPC supplanted anthracite as soon as CPC became commercially available due to its superior combination of electrical conductivity, resistance to chemical and physical degradation in the smelting pot, higher carbon content, and low contaminants. Titanium Dioxide: Calcined pet coke is used in the production of titanium dioxide (TiO2), a naturally occurring mineral used as a pigment for plastic, paint, sunscreen and food coloring. Two significant uses of titanium dioxide are as a substitute for lead in paint and as a whitener for paper.

Total: 32 MMT

Fig. 2 world petroleum coke consumption in 2016

III. INFLUENCE OF PARAMETERS AFFECTING ON CALCINED COKE QUALITY

A. Density

The differences outlined above have a significant impact on some calcined coke quality parameters. The most universally reported difference is the higher bulk and apparent density achieved with a shaft calciner. This is due to the slower heat up rate of green coke. The loss of VM creates porosity in coke. Lower VM gives lower porosity (and higher density) so lower VM green coke is always preferred. Porosity is also a function of the heat-up rate of the coke and this is a well known and
documented phenomenon [7,8]. Faster heat-up rates create higher porosity and lower bulk density.

B. Size

This is generally true with one significant qualifying comment. Shaft calcined coke has high levels of -75μm fines. This can result in significant dusting problems that have not been mentioned in previous papers and which is not obvious when one first looks at the coke. The lower heat up rate minimizes explosive shattering of large particles caused by rapid VM release. The coke bed moves very slowly through the shafts. In a rotary kiln, the coke is tumbled to improve heat transfer and consistency of calcination and this reduces the average particle size. Mechanical handling of the coke in screw conveyors, bucket elevators, conveyor belt transitions and silo’s also contributes to particle attrition in a rotary kiln calciner as previously reported [9,10].

C. Reactivity of coke and Impurity

Result between the ability of a rotary kiln or shaft calciner for RD targets are very similar. This is contrary to what has been reported in some other papers and is based on Rain’s experience with multiple rotary kiln and shaft calciners. When green coke quality changes significantly, it is easier and quicker to adjust a rotary kiln due to the high level of automation and multiple control variables available. There are also no fundamental differences in coke CO2 and air reactivity between the technologies. Coke reactivity is dependent on impurity levels in the coke (S, Ca, Na, V etc) and the level of calcination. Many aluminium companies have moved away from coke CO2 and air reactivity specifications because they typically show no or little correlation to anode CO2 and air reactivities [10,11].

IV. CONCLUSION

Petroleum coke is a by-product from crude oil refineries, but as its value represents only about 2 per cent of the overall production it has a limited interest to the producers. Mechanical and physical properties of coke are influenced by the crude oil, processes within the refineries and calcining of the coke. Shaft Calciners may remain to be an important element in China, but their market share will shrink with new bigger calciner plants that are building using rotary kiln technology. Continuous high demand for calcined coke by aluminium smelters has created a difficult situation with respect to quality and availability, leading to the use of lower quality coke in aluminium smelters and potential disturbances in the production. The carbon-hydrogen ratio is increased from a magnitude of 20 to 1000 when green coke is treated at 1200°C to 1450°C. Comparison between Rotary Kiln versus Shaft Calciner by Technip is shown in below items.

- Replacement of shaft furnaces is required within 5 up to 10 years from start of operation.
- Replacement of shaft furnace requires 6 months and shaft calciner require 2 months for startup times up; Rotary Kilns can be started up within a period of 3 days.
- Maintaining of clean fluewalls requires high level of manual maintenance work.

The calcined petroleum coke is a hard, dense carbon material with low hydrogen content and good electrical conductivity. These properties, combined with low metal and ash contents, make calcined petroleum coke suitable as a raw material for carbon anodes for the production of aluminium.

Use the rotary kiln cause the most efficient and most selected technology for petroleum coke calcining. They make an excellent bulk density product but dusting cans a problem.

REFERENCES