

Tutorial: Petroleum Coke Calcining and Uses of Calcined Petroleum Coke

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Prepared for presentation at the **AIChE 2000 Spring National Meeting**
Atlanta, GA
March 5-9, 2000

3rd International Conference on Refining Processes
Session T9005 - Tutorial: Delayed Coking

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ABSTRACT

Great Lakes Carbon Corporation founded the continuous petroleum coke calcining industry with the start-up of the company's first rotary kiln in 1935, the world's first rotary kiln used for the purpose of creating a product high in carbon purity for use in making anodes for aluminum smelting. This tutorial paper will describe the transformation of the petroleum coke calcining industry from the fledgling early days of the Great Depression to the competitive global industry of today. The coke calcining process will be described in detail. Modern calcining technology in use at a typical calcining plant will be presented. A summary of the properties desired for each of the uses of calcined petroleum coke will be included. Process overviews will be shown for each of the industries that use calcined petroleum coke including aluminum smelting, graphite electrode manufacturing, TiO₂ processing, chemical processing, and steel production.

WHAT IS PETROLEUM COKE CALCINING?

Petroleum coke is calcined (roasted at high temperatures, 1200 to 1350°C) usually in a gas-fired rotary kiln or rotary hearth to remove moisture, drive off volatile matter, increase the density of the coke structure, increase physical strength, and increase the electrical conductivity of the material. The result is a hard, dense carbon (calcined petroleum coke) with low hydrogen content and good electrical conductivity. These properties along with low metals and ash contents make calcined petroleum coke the best material currently available for making carbon anodes for smelting of alumina to aluminum.

HISTORY OF THE PETROLEUM COKE CALCINING INDUSTRY

The Early Days of Coking

A byproduct of petroleum refining, petroleum coke initially came from several different types of operations. From early refining with small iron stills to the horizontal batch stills of the 1860-1880's, through the introduction of the tube furnace and distillation columns in the 1920's, and thermal cracking process introduced in the 1920's, the delayed coking process was developed. In all of these early methods of refining and thermal cracking, petroleum coke was produced.

Batch Still Coking. Shortly after the discovery of crude oil in Pennsylvania, early "refineries" which boiled crude oil in small wrought iron stills to recover kerosene produced the first petroleum coke in the 1860's. The stills were heated by wood or coal fires built underneath which over-heated and coked the oil near the bottom. After the distillation was completed, the still was allowed to cool so the workmen could dig out the coke and tar before the next run [Conners 1981]. The early batch stills led to the use of single horizontal shell stills for distillation of crude oil which continued through the 1880's. Multiple horizontal stills were used to process more fractions by running the stills in series with the first still producing the coke. These horizontal stills were fired mostly with coal or some of the petroleum coke. Horizontal batch still coke was removed through an opening at the end of the horizontal tank with relays of men wrapped up in rags to protect against the heat using picks, shovels, and wheelbarrows. Horizontal batch still coke was 150 to 750 mm thick and had a glossy luster, low volatile matter (~8 wt%), low moisture (<1 wt%), ash content of ~1 wt%, and after removing was mostly lumps with only a small amount of fines.

In the 1920's, the tube furnace and distillation columns were introduced. Crude oil was heated in the tube furnace and proceeded to the distillation column. The bottoms (reduced crude or residuum) from the distillation column was charged to horizontal batch stills previously described. This produced a maximum amount of heavy gas oil. Some of these units were still in operation after World War II and required the same manual decoking as described above [Ellis and Paul, 1998].

Thermal Cracking. Vertical soaking drums were first used in the thermal cracking of gas oil for the production of gasoline and diesel fuel. In the 1920's, Dubbs at Universal Oil Products (UOP) developed a thermal cracking process to produce gasoline from heavy gas oil. This thermal cracking process was operated at higher pressures and coke was formed in a vertical soaking drum. The units

were called “Dubbs” units or cracking stills. The three meter (10 ft) diameter by 12.2 m (40 ft) high vertical soaking drum had a bottom manhole in which the coke was extracted. Over 1219 m (4000 ft) of steel cables 22 mm (7/8 inch) diameter were wrapped around inside the drum by hand and fastened to small ears on the drum walls. At the end of the thermal cracking run, the cables were pulled out to dislodge the coke. Any coke remaining on the walls was manually cleaned off before re-wrapping the cable inside the drum. This thermal cracking still coke had higher volatile matter, smaller sizing (contained a large amount of fines), and was considered to be a poor quality coke compared to the lumpier batch still coke [Swanson 1930].

Delayed Coking. The vertical cracking stills were the forerunners of the delayed coking process. The first “modern” delayed coker was built by Standard Oil at Whiting, Indiana in 1929. Delayed coking combined a number of the features and improvements from thermal cracking. The use of pressure as well as heat for cracking, separating the heater from the coke drums, and the use of two drums enabled the delayed coker to operate on a continuous basis. Lack of an adequate supply of crude oil and the lack of a heavy oil market caused land-locked Midwest refineries to process the heavy fuel oil (atmospheric distillation bottoms and vacuum distillation bottoms) in a delayed coker to produce more gasoline and diesel fuel. Decoking the drums was difficult. “Manual decoking was a hot and dirty job. ... Various mechanical devices were tried. One of the common systems employed was to wind several thousand feet of steel cable on holding devices in the drum. A cable was pulled with a winch to loosen the coke. Coke was also removed by drilling a small hole, then a large hole, after which beater balls on a rotating stem knocked out the remaining coke [Conners 1981].” The development of hydraulic decoking which uses high-pressure water pumped through a drill pipe and cutting bit to cut the coke from the drums came in the late 1930's. Standard Oil at Whiting was one of the early developers of hydraulic decoking.

The Growth of Delayed Coking versus Fluid Coking. The number of delayed cokers built from 1929 to 1955 was small, but a surge in delayed coker construction took place between 1955 and 1975 [Conners 1981]. The growth of delayed coking kept pace with the growth of fluid catalytic cracking and the rapid decline in thermal cracking. A fluid coker, similar to a fluid catalytic cracker except that fluid coke is circulated instead of catalyst, was first built in 1954 at Billings, Montana. Five more fluid cokers were built in the late 1950's, and one in 1970. In the late 1950's, some thought that all new cokers built would be fluid cokers [Ellis and Paul, 1998]. Due to the lower capital cost, delayed coking became and still is the coking process preferred by many refiners. Today there are 50 operating delayed cokers in the U.S. and only six fluid cokers / flexicokers.

Early Coke Marketing / Great Lakes Carbon Corporation

Great Lakes Carbon Corporation was formed originally as Great Lakes Coal & Coke Company by George Skakel, Sr. in partnership with Walter Gramm primarily to broker coal in 1919. Later in 1939, the company was incorporated as Great Lakes Carbon Corporation. In addition to trading coal, during the late 1920's, Great Lakes Carbon (GLC) became actively interested in petroleum coke. As you can recall from the previous sections, petroleum coke at this time was made by the horizontal batch still and thermal cracking still processes.

As thermal cracking processes became popular in the 1920's, the quantity of the thermal cracking still coke grew rapidly causing problems with disposal [Swanson 1930]. Mountainous storage piles of petroleum coke, amounting to several million tons, accumulated in Texas and adjacent coastal and interior refineries as well as at other refineries throughout the U.S. This petroleum coke with low ash content, <0.5 wt%, and a high heating value, ~37.1 J/kg (16,000 BTU/lb) resembled both bituminous mine coal and slot oven byproduct metallurgical coke. As a result of the lack of market for this new refining byproduct, the problem of petroleum coke storage became an acute one at many refineries. Petroleum coke created handling expense, took up valuable storage space within the refineries, and added to the fire hazards around the refineries [Watkins 1937].

In the early days, many refineries were often so desperate to get rid of petroleum coke due to the fire hazards and handling problems that some refineries actually paid GLC to take the coke off their hands. Refineries were very happy when they were able to sell the coke, even if it was for a low price. In 1932, GLC entered into handshake agreements with practically all of the refiners to purchase coke and concentrate its efforts on creating a market for petroleum coke. Large plants were constructed for cleaning, sizing, screening and transferring coke at port and rail terminals. These efforts resulted in completely liquidating the storage piles of what was a burdensome and practically valueless product [Watkins 1937]. Some of the early uses of petroleum coke were home heating and industrial heating (for the lumps) and burning with coal at power plants (for the fines). The biggest market was along the Atlantic coast, but this fuel coke market quickly spread to Europe and worldwide in a short time [Hardin and Gehlbach, 1992].

Birth of Continuous Petroleum Coke Calcining

In searching out uses for petroleum coke, it was found that certain foreign and domestic consumers required a material having the highest value of fixed carbon. The largest such market was for making carbon anodes for the aluminum industry. Calcined coal was being used as the carbon source at the time. To meet this demand for higher purity carbon, GLC installed a unique plant in Port Arthur, Texas using raw petroleum coke as its raw material [Watkins 1937].

Before 1935, some petroleum coke was calcined batch-wise in slot ovens similar to units used to calcine coal. Attempts had been made at calcining petroleum coke (lump only) in vertical shaft kilns by passing hot combustion gases up through a moving bed of coke, but there were many problems with this type of system. A small amount of coke was calcined in electric furnaces, but this was an expensive process [Hardin and Gehlbach, 1992]. GLC hired a professor from the University of Illinois in 1934 who thought that petroleum coke could be continuously calcined in a rotary kiln similar to kilns being used in the lime and cement industries.

In the middle of the Great Depression, GLC decided to test the idea and purchased a used lime kiln in Canada. The kiln was shipped to Port Arthur, Texas on a barge through the inter-coastal waterway and was set up on waterfront property leased from the railroad. Several million tons of raw petroleum coke were on the ground at a nearby Texaco refinery. The rotary kiln was started up in October 1935 becoming the first rotary kiln in the world to continuously calcine petroleum coke. The calcined coke was stored in an old wooden cotton storage shed. Loading calcined product in the first ship in 1936

was a very labor-intensive process. Workers loaded wheelbarrows by hand and pushed them up gangplanks to the ship.

Growth of the Petroleum Coke Calcining Industry

As the use of calcined petroleum coke in making anodes for the aluminum industry was proven commercially, the demand for calcined coke escalated dramatically. GLC built new kilns and calcining plants at a very rapid pace with six new kilns coming on-line from 1937 to 1943. Growth in delayed coker construction from 1955 to 1975 also fueled the growth of petroleum coke calcining into the early 1970's with eleven more GLC kilns starting up from 1952 to 1972. A few competitors (refiners, aluminum smelters, and other independent calciners) also began to build calcining plants to enter the anode grade calcined petroleum coke market in the 1950's.

“Needle Coke” Calcining / Graphite Electrodes. Another development in the 1950's that spurred the growth of petroleum coke calcining was the development of synthetic graphite from a special kind of petroleum coke called “needle coke”. GLC discovered and patented [Shea 1956] this special petroleum coke that could be produced by delayed cokers and calcined for use in making graphite electrodes used in steel arc furnaces. As steel mini-mills became popular, a rise in demand for graphite electrodes and green needle coke prompted many refiners to produce needle coke in blocked operations. Specifications for needle coke are quite stringent and require special coking and special calcining as is described later in this paper. Early on some refiners, and later, independent coker/calciners and steel producers (mostly in Japan) were able to enter the calcining industry to produce needle coke.

As crude oil supplies to refineries began to increase in sulfur in the 1970's, many refiners were unable to meet the sulfur specifications for (high quality) non-puffing needle coke and were gradually forced out of the market. As some of the refiners left, a few independent coker/calciners entered the industry to capture this niche market by coking special coker feedstocks that could still meet needle coke specifications. As graphite electrode quality improved and mini-mills became more efficient in their use of graphite electrodes, the demand for calcined needle coke decreased in the late 1980's. This downturn in demand caused a few players to drop out, but enabled the remaining participants to actually increase production and remain competitive. Today, all the producers of premium green needle coke also calcine their own coke.

Petroleum Coke Calcining Industry Today. Today, a fiercely competitive global petroleum coke calcining industry exists. GLC, the world's largest producer of calcined petroleum coke (CPC) with production capacity of over 1.6 million tons, has nine operating rotary kilns at three locations: Port Arthur, Texas (4 kilns); Enid, Oklahoma (3 kilns); and La Plata, Argentina (2 kilns). In the total industry, approximately 30 producers of CPC include refiners, smelters, independent calciners, independent coker/calciners, graphite electrode manufacturers, and steel producers. Global expansion of the industry has resulted in the establishment of calcining operations in Canada, Argentina, Brazil, United Kingdom, Germany, Norway, Spain, South Africa, the Middle East, India, Indonesia, Japan, China, and Russia [Martinez and Bartholomew, 1998].

MODERN CALCINING PROCESS AND TECHNOLOGY

There are two primary methods of continuous calcination of petroleum coke, the rotary kiln and the rotary hearth furnace. These two methods are described in detail in this paper. To our knowledge, there is only one other method in use today for calcining coke. Located in Russia, it is a special type of heated wall vertical shaft calciner (sort of like a moving slot oven) that can produce a good density coke. The operating cost is higher than a rotary kiln or hearth, but the slower up-heat rates allow them to use higher volatile matter green coke to achieve similar calcined densities.

Rotary Kiln

Kiln. Most petroleum coke is calcined in a rotary kiln. A schematic of a coke calcining plant using a rotary kiln is shown in Figure 1 [Bagdoyan and Gootzait, 1985]. A rotary kiln is a rotating horizontal cylinder 2.5 to 5 meters in diameter and 50 to 80 meters long lined with 0.23 m thick special high-temperature refractory brick. The kiln shell is made of steel 25 mm thick with the section under the kiln tires 50 to 75 mm thick. The kiln shell is supported by the tires, which ride on two wheels or trunions. The kiln is rotated via a large bull gear that is larger than the circumference of the kiln shell and is driven with one or two spur gears. The spur gears are driven through a gearbox by either direct electrical drive or by hydraulic motors. The electrical drive speed is varied by either a varying frequency or through an eddy current type clutch.

Calcining Process Flow. Raw petroleum coke is sized to 50 to 100 mm lump and fed to raw feed silos, then to the rotary kiln (at the high end) through a side feed scoop or through a feed pipe (in older units). The kiln is sloped downward towards the discharge end at a slope of 13 to 19 mm per 300 mm ($\frac{1}{2}$ to $\frac{3}{4}$ inch per foot). As the coke progresses down through the kiln countercurrent to the hot combustion gases, the temperature increases to a maximum temperature that is reached around 13 to 20 m before the discharge end of the kiln. After entering the kiln, moisture is driven off the coke in the “Heat-Up Zone.” Devolatilization occurs mostly at 500 to 1000°C in the “Calcining Zone.” Further dehydrogenation, some desulfurization, and coke structure shrinkage (densification) take place in the “Calcined Coke Zone” at 1200 to 1400°C (see Figure 2). The coke moves through the kiln in 40 to 60 minutes and drops off the discharge end of the kiln into a refractory-lined chute and into a rotary cooler.

Cooler. The cooler is a bare steel cylinder similar to the kiln but usually smaller in diameter, shorter, and rotated at higher rpm's than a kiln, with water sprays in the front end. Water is sprayed to contact the hot coke, taking advantage of the very high latent heat of vaporization of the water for cooling. Indirect water-cooled rotary cylinder coolers are used where poor water quality prevents the use of direct cooling. The coke spends about 20 minutes in the cooler and is discharged onto high temperature conveyor belts or into screw feeders. Computer controls adjust the water sprays to maintain the coke at the cooler exit at ~120 to 180°C (250 to 350°F) in order to keep the calcined product dry.

Firing Crown and Heat Transfer. At the discharge end, the rotary kiln has a burner in the firing crown (a hood that fits over the discharge end of the kiln) to preheat the refractory before

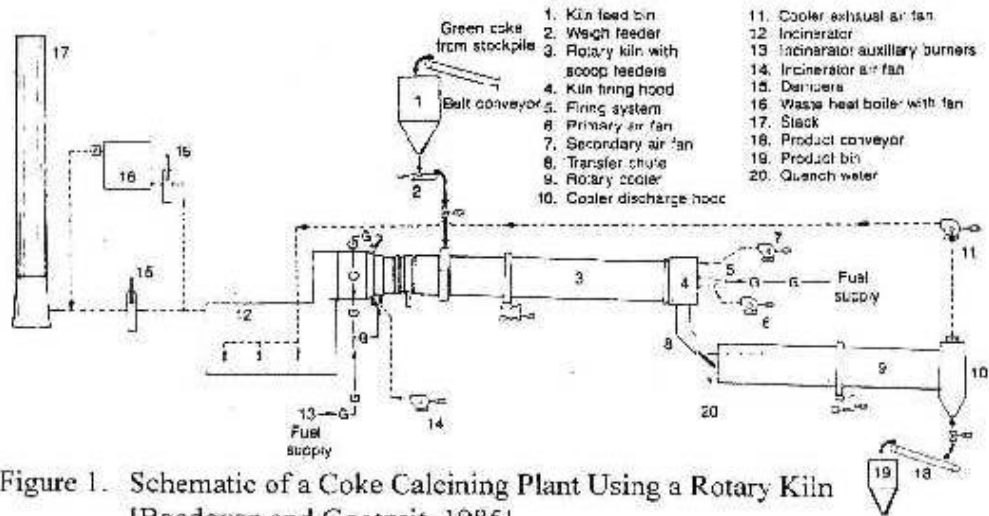


Figure 1. Schematic of a Coke Calcining Plant Using a Rotary Kiln [Bagdoyan and Gootzait, 1985]

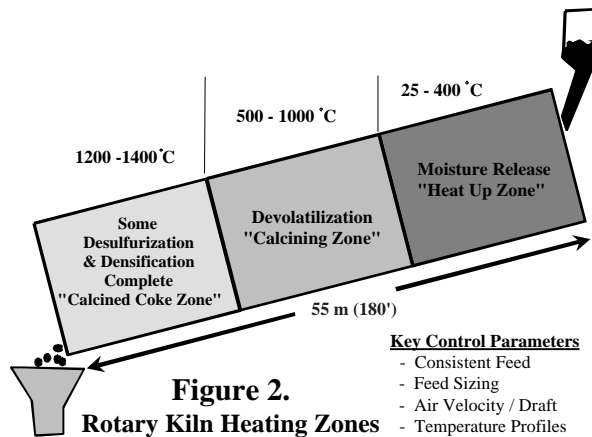


Figure 2. Rotary Kiln Heating Zones

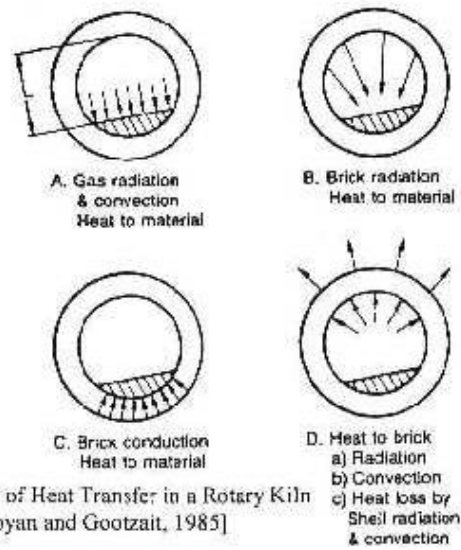


Fig. 3. Modes of Heat Transfer in a Rotary Kiln [Bagdoyan and Gootzait, 1985]

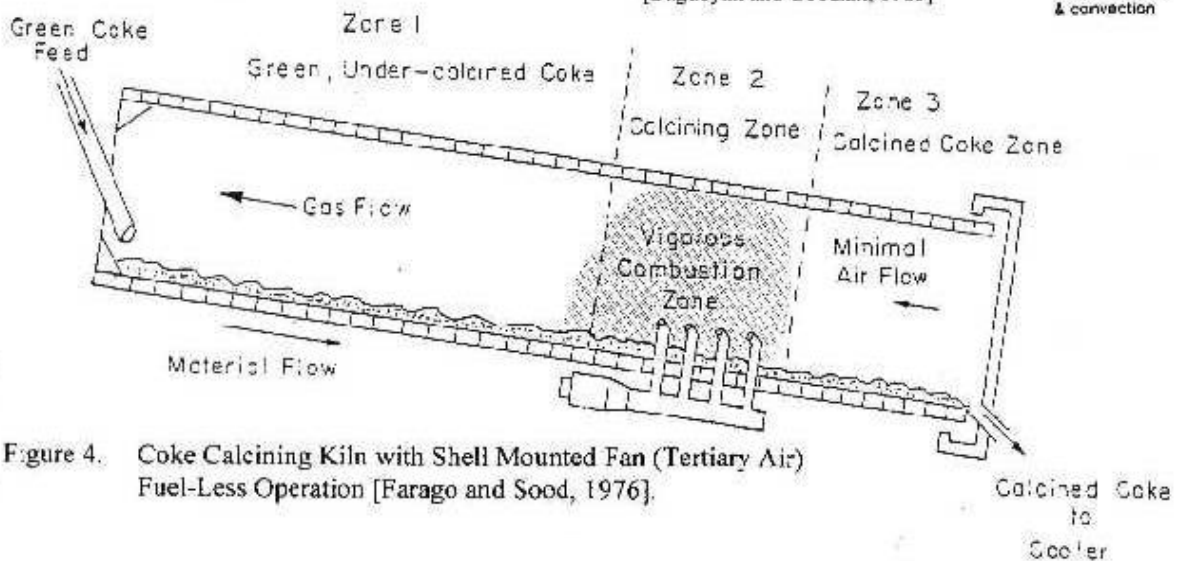


Figure 4. Coke Calcining Kiln with Shell Mounted Fan (Tertiary Air) Fuel-Less Operation [Farago and Sood, 1976].

start-up and to supply some of the heat for calcining in most applications. Most kiln burners are natural gas fired, but some older model kilns have oil-fired burners. Combustion air is also injected through the firing crown. Some kilns use oxygen instead of air to reduce combustion gas flows and to decrease or eliminate the need for gas firing. The temperature in the kiln is monitored by an optical pyrometer focused on the discharging hot coke. The temperature is controlled by the amount of gas, excess combustion air, kiln rotation speed, and raw coke feed. As depicted in Figure 3, almost all of the heat transfer to the material is by radiation from kiln gases and exposed portions of refractory wall, and by convection from gas. A small amount of heat is transferred by conduction from the refractory to the material [Bagdoyan and Gootzait, 1985]. Analysis of either the real density or the electrical resistivity of the calcined coke measures the degree of calcination.

Incinerator (Pyro-Scrubber). Water vapor (from moisture of the raw coke), hot combustion gases, unburned entrained coke fines, and unburned tars and gases (from the volatile matter of the raw coke) flow out the feed end of the kiln into a hot incinerator or pyro-scrubber where excess fuel and fines are burned. The incinerator (also called a combustion or settling chamber) is operated with a negative pressure so that the kiln also operates under a slight negative pressure. Either a tall stack or an induction fan produces the negative pressure in the incinerator if waste heat boilers (downstream of the incinerator) are used.

Tertiary (Shell) Air Injection. Since volatile matter coming off the coke during calcination contains around twice the fuel value required for calcining, it is logical to attempt to burn this fuel for calcining. Tertiary air (air injected through the side of the kiln from shell mounted blowers) forms a second hot zone in the kiln that extends up toward the feed end of the kiln (see Figure 4) by burning this volatile matter as fuel. Many rotary kilns use tertiary air for the main advantages of increased production rates and decreased consumption of natural gas. The major disadvantage of using tertiary air is that a faster up-heat rate in the critical range of 500 to 700°C with tertiary air [Brooks 1989] may result in poorer coke quality (vibrated bulk density) than without tertiary air. The original inventor of tertiary air injection is believed to have abandoned the idea for this very reason.

With special kilns and special operating practices it is possible to use tertiary air injection to produce calcined coke of adequate quality for use in making carbon anodes. Alcan has much experience in the use of tertiary air and claim to calcine petroleum coke without burning any natural gas (after start-up). The Alcan kilns are long, 61 meters, and small in diameter, 2.43 m. Tertiary air is injected 20 m (1/3 kiln length) from the discharge end. Smaller slopes and higher rotational speeds are used than those of conventional kilns in order to increase coke bed depth and increase agitation of the bed for a more uniform up-heat rate of the coke [Farago and Sood, 1976].

Rotary Kiln Operation. Some of the key control parameters for operating a rotary kiln to produce good quality calcined coke include control of the up-heat rate of the raw coke and raw coke feed consistency and sizing.

Slow Up-heat Rate is Critical. The primary objective in calcining petroleum coke for the aluminum industry is to slowly heat the coke during the initial devolatilization around 500 to 600°C so that the mesophase or liquid crystal part of the coke does not bloat or distort (pop-corn)

during the evolution of the volatile matter. Petroleum coke with anisotropic (needle) structure and/or high volatile matter must be calcined with slow up-heat rates in order to produce good calcined densities and low porosity.

Lifters. Some attempts have been made using “lifters” in kilns to increase production and keep the coke up-heat rate down by stirring the coke bed [Kaiser Aluminum 1983]. Lifters are castable refractory or refractory bricks that stick up above the surrounding bricks. The exact location for lifters to decrease coke up-heat rate especially in the critical 500 to 600°C range is not known for all kilns. There is also a great problem with keeping lifters in a rotary kiln. Refractory bricks and the steel shell of a rotary kiln both expand. Bricks must expand enough so that they are not too loose in the kiln to prevent excess walking yet not so tight as to exceed the hot crushing strength of the brick. Lifters get hotter at their tips, have a pinch point at the interface of the surrounding bricks, and are subject to breaking at the interface. Several complete rings of taller bricks seem to hold together, but the adjacent bricks on the upside become worn out due to a stagnant layer of coke that grinds down the bricks. Lifters can also cause other problems when a coke bed is stirred too much such as entrainment of fines in the exiting combustion gases.

Feed Consistency and Sizing. The degree of coke calcination depends mostly on variations in the raw coke such as differences in structure, volatile matter, and particle sizing. In rotary kilns, it has been documented that coarse particles travel faster through the kiln than the finer particles. Some calciners have stated that coarser coke with lower quantities of fines can increase the production rate in a kiln (enabling more tons per hour to be calcined). Without proper sizing and feeding of a rotary kiln, slides can occur dumping most of the material rapidly out of the kiln. Rapid devolatilization in the calcining zone tends to fluidize the coke (observed in the GLC shaking-hearth pilot calciner). A large amount of fines in the calcining zone all at once fluidizes more readily, causing the slides.

Rotary Hearth

The other commercial method of calcining petroleum coke is with a rotary hearth calciner. Marathon Oil and Wise Coal and Coke Company jointly developed the rotating hearth furnace for calcining coal and then adapted the technology for calcining petroleum coke [Merrill, Jr. 1978]. The first rotary hearth calciners for petroleum coke were located in Europe. A simplified process flowsheet for a rotary hearth calciner operation and an elevation view are shown in Figures 5 & 6.

The rotary hearth consists of a large rotating disk-type furnace that slopes from the outside toward the center. Raw coke is fed into the outer edge of the rotary hearth and is plowed inward with water-cooled plows called rabblers that push the coke toward the center (see Figure 7). The rabblers can be adjusted to control the coke bed depth leaving enough stagnant coke to prevent wear of the refractory. Coke fines usually sink down into the coke bed thus eliminating any entrainment with the combustion gases above the coke bed. The stirring of the coke bed is critical for good heat transfer so that all coke can reach calcination temperature. After passing through a center soaking pit, the hot coke falls through a rotating discharge table into a cooler [Allred 1971; Merrill, Jr. 1978].

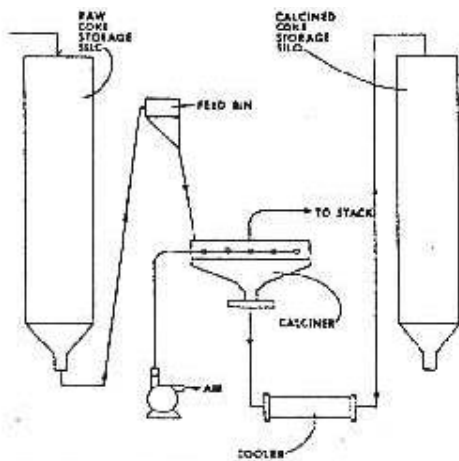


Figure 5. Simplified Process Flow Sheet
Rotary Hearth Calciner Operation.

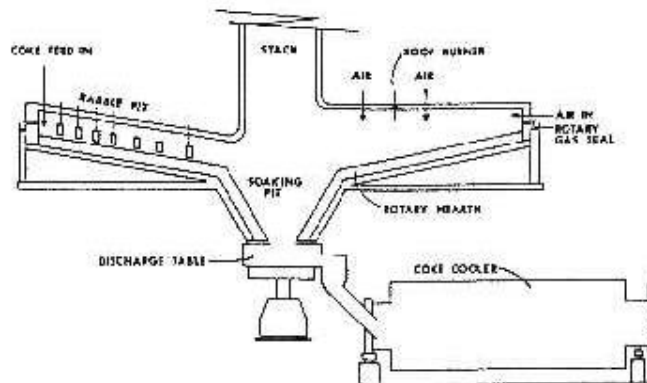


Figure 6. Elevation View of Rotary Hearth Calciner.

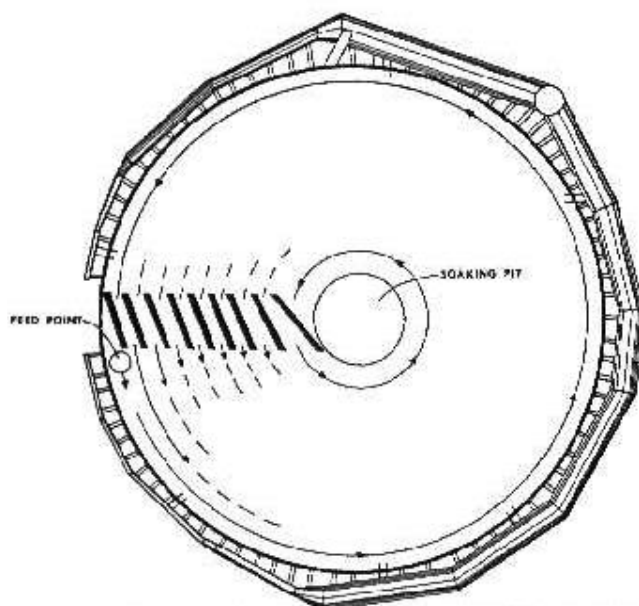


Figure 7. View Showing Coke Movement Across Rotary Hearth

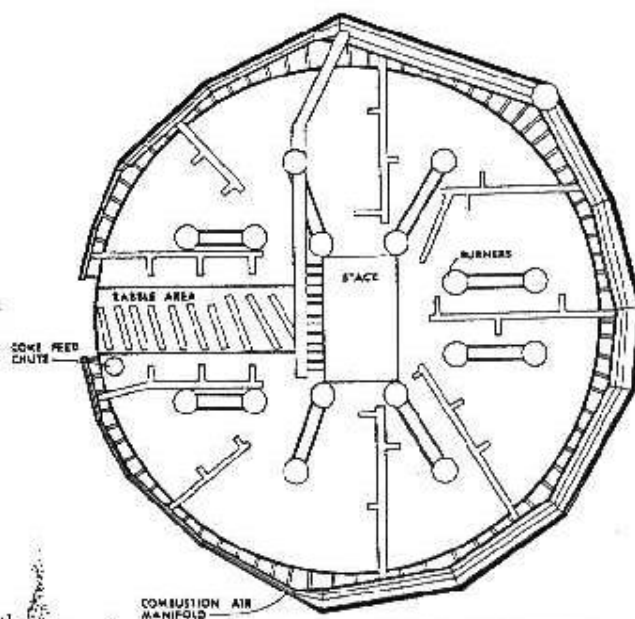


Figure 8. Plan View of Rotary Hearth Calciner
Showing Air Distribution and Burner
Systems.

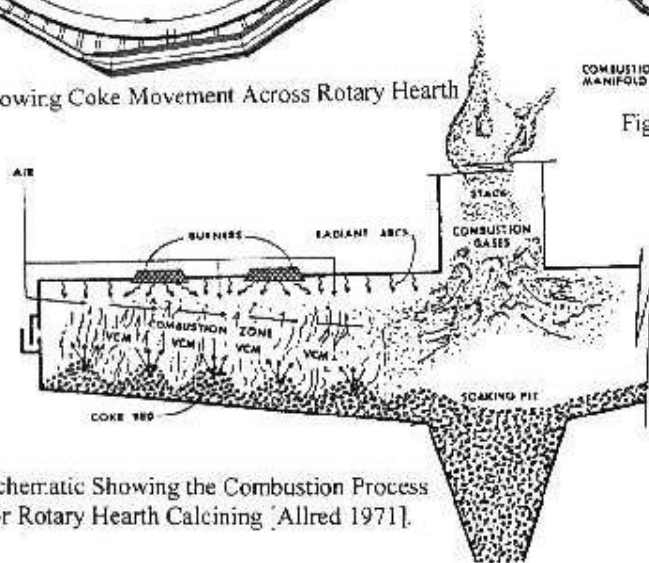


Figure 9. Schematic Showing the Combustion Process
for Rotary Hearth Calcining [Allred 1971].

Burners and combustion air nozzles are located on a stationary, suspended roof (see Figure 8) that is connected to the rotating hearth with a seal between the two. After start-up, the rotary hearth calciner makes use of the complete combustion of the volatile matter of the raw coke feed. Little or no excess fuel is required for heat. The hot combustion gases coming off the top center of the roof are used to preheat the combustion air in some hearths to further improve combustion efficiencies. The small amount of coke fines and the volatile matter from the coke are completely consumed in the roof of the hearth, so no external incinerator is required. A schematic of the combustion process in a rotary hearth calciner is shown in Figure 9.

Rotary Hearth Advantages Over Rotary Kiln. Some advantages of a rotary hearth calciner are:

- 1) Reduced Refractory Cost - Since the refractory on the hearth is covered with a layer of coke, there is very little wear. Refractory on the top of the kiln is stationary, eliminating problems with brick lock and rotating forces that are present in a rotary kiln.
- 2) Lower Particulate Emissions - The coke fines are not entrained into the kiln exhaust.
- 3) Reduced Heat Losses / Less Fuel Consumption - Little or no extra fuel is required if combustion air is preheated.
- 4) Elimination of Exterior Combustion Chamber for Incinerating Fines and Volatile Matter - Complete combustion occurs within the calciner.
- 5) Variable Operation - Varying the turntable speed and coke bed depth can change operating conditions and residence time over a wide range.

Disadvantages. Some of the major problems with rotary hearth calciners has been with the rapid up-heat rate of the coke and calcined coke particle sizing. Rapid up-heat of the coke causes coke structure to become bloated, distorting the structure of the coke. This leads to poor bulk densities for the calcined product. Some of the newer rotary hearth calciners use a special shadow wall near the raw coke inlet to help reduce the up-heat rate of the coke. Due to the nature of the material movement through the rotary hearth, less coke fines are burned up or lost in the flow of the combustion gases. Although this keeps particulate matter out of stack emissions, the fines remain in the calcined product causing difficulties in meeting sizing specifications for anode grade coke. Too many fines in the product can also cause fugitive dust problems when handling the product.

DESIRED PROPERTIES OF CALCINED COKE

Volatile matter (VM) in raw petroleum coke prevents its use in making carbon anodes with good density, strength, and electrical conductivity. Small carbon bodies can be processed from raw coke for some uses, but these require very elaborate processing with extremely slow up-heat rates. Therefore, most uses other than for fuel or gasification require raw coke to be calcined in order to improve its properties. Changes that occur in the physical and chemical properties of petroleum coke

during calcination include decreases in VM, hydrogen, sulfur (slightly), electrical resistivity, air and CO₂ reactivities, and d-spacing, and increases in density, crystallite thickness (L_c), and most metal contents (concentration due to loss of VM). Some general specifications for raw and calcined petroleum coke to be used for making anodes for aluminum smelting are shown in Table 1. These properties are described in detail in the sections that follow.

Table 1. General Specifications for Anode Grade Coke

Properties	Petroleum Coke	
	Raw	Calcined
Moisture, wt%	8-10	< 0.30
Hydrogen, wt%	----	< 0.10
Ash, wt%	< 0.40	< 0.40
VM, wt%	< 11.5	< 0.40
Sulfur, wt%	< 3.5	< 3.0
V, wppm	< 300	< 250
Ni, wppm	< 200	< 200
Si, wppm	< 250	< 200
Fe, wppm	< 300	< 300
Ca, wppm	< 200	< 150
Na, wppm	< 100	< 100
Shot Coke Content, %	0	0
Vibrated Bulk Density (VBD), g/cc	----	> 0.84
Apparent Density (Hg), g/cc	----	> 1.70
Real Density (He), g/cc	----	2.050-2.080
Electrical Resistivity, ohm-in	----	< 0.042
Air Reactivity @600C (Fast), %/min	----	< 0.25
Air Reactivity @525C (Slow), %/min	----	< 0.30
CO ₂ Reactivity, %	----	< 12.0
Grain Stability, %	----	> 75
Pulverization Factor	----	0.9-1.1
Hardgrove Grindability Index (HGI)	75-85	32-40
Sizing: Screen Test, Cumulative%		
+30 mm	----	0.0
+8 mm	----	> 8.0
+4 mm	----	30-40
+2 mm	----	> 45
-1 mm	----	< 30
-0.25 mm	----	< 15

Physical Properties

Real Density (RD). The real density (RD) of raw or green coke is 1.3 to 1.4 g/cc (measured on minus 200-mesh particles using a helium pycnometer), and after calcination, anode grade coke is usually calcined to around 2.05 to 2.08 g/cc. Calcined needle coke for graphite electrodes can reach RD's of 2.13 g/cc. In low sulfur coke, RD increases as temperature increases, so this property is commonly used to control the calcining operation. For higher sulfur coke, increasing temperatures

beyond 1250 to 1300°C can actually decrease RD due to desulfurization which creates small pores in the coke [Rhedeý 1967; Hardin et al., 1993].

Electrical Resistivity. The electrical resistivity of calcined coke decreases with increasing calcination temperature. An empirical method was set up to measure the resistivity of sized coke particles in a ceramic cylinder with pressure (150 psi) loaded silver-plated brass rams on either end of the cylinder [Hardin et al., 1994]. Petroleum coke actually changes from an insulating material into a conductor upon calcination [Hardin and Gehlbach, 1992].

Hg Apparent Density (AD). The mercury apparent density (AD) is a measurement of porosity and density. Anisotropic, needle-type coke structure produces higher AD upon calcining than isotropic, sponge or shot coke structures. According to Hardin et al. [1994], calcining above 1250°C decreases AD for all coke samples with the exception of one low sulfur coke that did not decrease in AD until 1350°C. AD decreases very rapidly in high sulfur coke with the onset of desulfurization.

Vibrated Bulk Density (VBD). Vibrated bulk density (VBD) of calcined coke is critical for use in the aluminum industry and is measured on a screened particle fraction. GLC uses 100 g of screened 20 to 48 mesh calcined coke particles vibrated in a graduated cylinder to determine VBD. The calcined coke for most prebaked anodes must have a density of 0.84 to 0.86 g/cc or higher by this method. Other test methods sometimes use other size particles such as 28 to 48 mesh or 8 to 14 mesh. The prebaked anode density correlates with the VBD of the calcined coke. Monitoring the quality of the green coke is the predominant control of the calcined coke VBD.

Low up-heat rates in calciners can improve VBD. Rhedeý [1967] stated that porosity increases if the up-heat rate is greater than 50°C/min. An increase in porosity of calcined coke decreases VBD. Hardin et al. [1993] shows that increasing calcination temperature to 1300°C increases VBD. Beyond 1300°C, VBD decreases.

Predicting VBD. GLC has correlated raw coke VM and CTE (Coefficient of Thermal Expansion) measured on a coke (calcined, ground to flour, mixed with coal tar pitch, extruded, into small rods, baked, and graphitized to 2900°C) with the calcined coke VBD. The CTE of a coke is a numerical measurement of the structure of the coke. Needle coke has very low CTE, $< 3 \times 10^{-7}$ cm/cm/°C; most sponge coke ranges from 6 to 18; and shot coke is usually over 20. Isotropic coke (shot-type coke) at a given VM will calcine to a higher VBD than anisotropic (needle-type) coke. With an estimate or measured value of the CTE of a raw coke, the VM/CTE/VBD correlation can accurately predict the VBD that would be produced from a range of raw coke VM values for a given raw coke supply.

Bloating. The reason that anisotropic (needle-type) coke has a tendency to produce lower VBD is that the mesophase part of the coke is in large domains and can be observed with an optical microscope [Whittaker and Grindstaff, 1972]. Since the mesophase domains have small diameters in isotropic coke, when this rigid skeleton is heated, the escaping volatile matter gases have a less detrimental effect on the coke structure. In anisotropic coke, the mesophase is in large

domains. When heated, the mesophase becomes plastic and is easily bloated or distorted by the escaping VM gases resulting in poor VBD.

Hardgrove Grindability Index (HGI). Hardgrove Grindability Index (HGI) is a measurement of the hardness of a coke and can be measured on both the green coke and the calcined coke. This property is most useful for green coke and is important for fuel grade coke that needs to be crushed for burning in power plants. The test uses a sized fraction 14 to 28 mesh that is placed in a grinding apparatus using two rotating disks with a groove that contains the coke and steel balls. Weight is placed on the disks, and the apparatus is turned for 60 revolutions. The coke is then retrieved and the amount of minus 200-mesh material present correlates with an HGI value. The test originates from testing coal with the HGI values corresponding to those of a set of coal standards. The HGI value provides a rough double-check for the VM test on raw coke when comparing coke samples of similar structures. Higher values (usually also high in VM) indicate that the coke is soft or more grindable. HGI is also influenced by coke structure with raw shot coke as low as 28 to 50 HGI and raw needle coke as high as 70 to 100 HGI. Raw coke HGI has been correlated to estimate VBD of the calcined coke. Raw coke HGI values 75 to 85 or lower are desired to produce good VBD calcined coke.

HGI is determined on calcined coke for some customers. Calcined coke HGI usually ranges from 32 to 40 and provides a rough measure of the hardness of the calcined coke. With such a tight range of values, HGI results for calcined coke are not as meaningful as results for raw coke, but the lower the value, the harder the coke.

Pulverization Factor (PF). An offshoot of the HGI for calcined coke is the Pulverization Factor (PF). PF uses the same apparatus as the HGI, but more revolutions are made with the disks. The value is calculated differently, but as with HGI, PF results in a measure of the hardness of the calcined coke, the lower the value, the harder the coke.

Grain Stability. Grain stability provides a measure of how well sized calcined coke particles 4 to 8 mm hold up under stress. Two 100 g samples of particles are placed with steel balls in two pots that are shaken together on an apparatus at 1470 RPM for 3.5 minutes. The amount of the particles remaining in the 4 to 8 mm size range is the grain stability. Hard particles (high values) are desired to withstand handling without breaking at the carbon anode plant.

Crystallite Thickness (L_c) and Interlayer Spacing (d-spacing). L_c is a measurement of the mean crystallite thickness in the carbon. This value increases with increasing calcination temperature. The d-spacing is the distance between the carbon planes, and d-spacing decreases with increasing calcination temperature. The L_c and the d-spacing appear to have the best correlation to calcination temperature of any single calcined coke properties. With high sulfur coke and high temperatures, Hardin et al. [1994] found that the rate of change was slightly increased at temperatures above 1350°C. This was thought to be due to internal pressure from sulfur evolution.

Air and CO₂ Reactivities. Reactivities of calcined coke in air at two different up-heat rates and in CO₂ are determined to provide information as to how an anode will behave in a smelting pot.

For air reactivity, weighed samples are placed under a purge of air and heated until ignition of the sample takes place. The ignition temperature is converted to a reactivity value expressed as %/min. A thermogravimetric method may also be used to determine the air reactivity. Samples for CO₂ reactivity are weighed and put in a purge of CO₂ while the sample is heated automatically to 1000°C. After cooling, the sample is weighed back to determine the percent of the sample that reacted. Calcining temperatures and the resulting coke densities (RD, AD, and VBD) and resistivity affect the degrees of air and CO₂ reactivities of the calcined coke. Metals such as Na, Ca, and V, catalyze both air and CO₂ reactions while sulfur tends to inhibit the CO₂ reactions.

Screen Sizing. Aluminum smelters require strict specifications on the amount of different size fractions of calcined product. To make carbon anodes, the calcined coke is first screened in the carbon plant to separate out different size fractions in order to recombine them with pitch (and recycled anodes or butts in prebaked anodes) in a desired paste recipe to produce the optimum anode density. Factors that influence the size of the calcined coke are the size of the raw coke supplied to the calciner and the handling steps required to load and deliver the product to the customer. Delayed coker operating parameters, coke cutting methods, and coke handling methods at the refinery all affect the size of the raw coke.

Shot Coke Content. Shot coke cannot be used for making anodes in aluminum smelting. Shot coke balls are made of two layers of material with different CTE values. These small balls (2 to 4 mm in diameter) fracture at the interface of the layers when calcined due to the differences in CTE of the two layers. The layers of the shot particles lead to cracks in the anodes since pitch binders adhere to only the outer layer of the particles [Ellis and Bacha, 1996]. Special segregation and handling practices are used at calcining plants to prevent contamination of anode grade raw coke with shot coke. A visual inspection test is used as needed to inspect anode grade calcined product samples for shot content. Some shot coke is calcined for use in non-anode applications.

Chemical Properties

Volatile Matter (VM). Volatile matter (VM) is a weight loss upon heating test measured on minus 60-mesh coke. The coke is placed in a covered platinum crucible that is lowered into a 950°C furnace at a prescribed rate of descent with intermittent stops. Volatile matter of raw coke usually varies from 8.5 to 12.5 wt%. Less than 0.4 wt% VM remains after calcining. In calcining processes, devolatilization usually starts around 500°C and is completed at 900 to 1000°C [Rhede 1967].

VM of raw coke is correlated to the VBD of the calcined product as described in the earlier section on VBD. Some VM from the raw coke is burned during calcination and accounts for some of the calcining yield loss. At VM levels above 12 wt%, a soot ring or “coke ring” can form and gradually build up at the feed end of the kiln. If enough of this “coke ring” builds up, the raw coke feeder can become blocked shutting down production.

Hydrogen. Hydrogen content is determined by combustion in oxygen. This property provides a measure of calcination of the product. Hardin et al. [1994] found that most of the

hydrogen evolves before 1000°C (<0.1% H in the product coke), but in one coke sample hydrogen evolution continued to 1275°C.

Moisture and Ash. Moisture and ash are measured by oven drying and muffle furnace ashing of the raw and calcined coke. The calcined coke must be dry to avoid problems with screening and fabrication of carbon anodes at the carbon plants of the aluminum smelters. Ash values usually fall in a typical range, 0.1 to 0.3 wt%. Higher than usual ash may indicate the presence of some type of contaminant in the coke.

Sulfur and Metals: V, Ni, Si, Fe, Ca, Na. Sulfur and metals contents are determined by XRF or ICP methods to assure that raw material and calcined products meet GLC and GLC customer specifications. In aluminum smelting, any excess metals in the coke travel to the aluminum since the coke (carbon anode) is consumed during the process. Some grades of aluminum metal require very low values of certain metals depending on the uses of the aluminum. Sulfur and some metals also affect the air and CO₂ reactivities of the calcined coke as mentioned earlier. Metals in the raw coke normally increase upon calcining due to the weight loss from evolution of the volatile matter, hydrogen, sulfur, and nitrogen.

During calcination up to 1350°C, some coke desulfurization (10 to 15%) usually occurs. Higher sulfur coke samples can have higher degrees of desulfurization (> 15%), and some low sulfur coke samples may remain unchanged up to 1400°C and show only a very slight decrease in sulfur beyond 1400°C [Hardin et al., 1994]. Literature suggests that nearly complete desulfurization could take place at 1600°C [Al-Haj-Ibrahim and Morsi, 1992]. Operating limits of today's calcining technologies prevent such high temperatures from being achieved economically, and the desulfurized product would have limited applications due to poor densities that would result.

Nitrogen – “Puffing” of Needle Coke. Nitrogen can be tested by a Leco combustion method or by micro Kjeldahl technique. The Kjeldahl method will determine the nitrogen that is complexed in the coke and not on the surface, but the digestion of the coke in sulfuric acid is very slow, taking several days. Nitrogen is not usually tested for anode grade calcined coke, but it is an important value for calcined needle coke and for certain steel applications.

Sulfur and nitrogen in calcined needle coke cause problems with “puffing” or the swelling or bloating of coke in the green electrodes during graphitization. Sulfur and nitrogen are evolved during calcination from 1200°C to 1800°C with the peak for sulfur being around 1400 to 1600°C. In low sulfur needle coke, a GLC dynamic puffing test would show puffing around 1800°C continuing through 2300°C indicating that sulfur and/or nitrogen was still being driven off. In higher sulfur and nitrogen coke, the majority of the sulfur and nitrogen may evolve at lower temperatures depending on the molecular structure of the sulfur and nitrogen compounds.

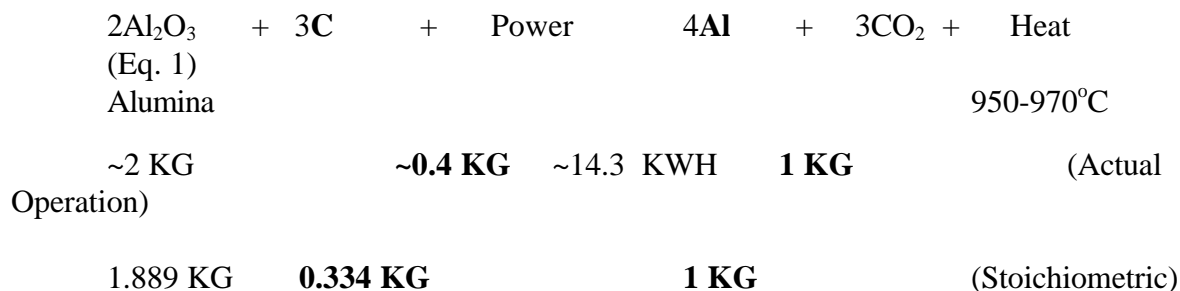
USES OF CALCINED PETROLEUM COKE

The primary use of calcined petroleum coke (CPC) is in making carbon anodes for the aluminum industry. CPC is also used in making graphite electrodes for arc furnaces, titanium dioxide, polycarbonate plastics, steel (to increase carbon levels), carbon refractory bricks for blast furnaces, packing media for anode baking furnaces, and material for cathodic protection of pipelines. The total production of all forms of raw or green petroleum coke in the world is around 44 million (MM) tons per year (TPY). The total world CPC production is ~10 MM TPY. Aluminum smelting uses ~7 MM TPY; roughly 1 MM TPY of calcined needle coke are used for graphite electrode manufacturing; and ~2 MM TPY are used for other uses such as for making titanium dioxide, steel (to increase carbon levels), and carbon monoxide for polycarbonate plastics.

Aluminum Smelting

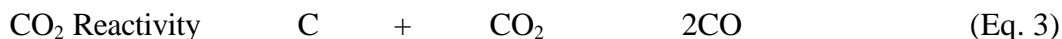
Aluminum is obtained by the electrolytic reduction of aluminum oxide (Al_2O_3) or alumina to elemental aluminum as shown in Equation 1 below. Electrolysis is performed by passing DC current through a molten electrolyte bath containing dissolved alumina. The electrolyte is primarily cryolite or sodium aluminum fluoride with some potassium aluminum fluoride and sodium aluminum tetrafluoride. The combination of these constituents influences the melting point, alumina solubility, conductivity, and viscosity of the electrolyte bath. The ratio of sodium fluoride to aluminum fluoride known as the “bath ratio” is monitored on a daily basis. Alumina along with aluminum fluoride or sodium fluoride (to maintain the bath ratio for maximum electrical efficiency) is added to the reduction cells by point feeders on a regular basis.

The electrolyte bath usually operates at 950 to 970°C (1742 to 1778°F). Carbon is currently the most suitable material that can be processed into an anode capable of withstanding and remaining inert to the hostile environment of the molten electrolyte and aluminum [Hardin and Gehlbach, 1992]. The carbon anode is primarily consumed by electrolytic oxidation. The oxygen from the dissolved alumina is released at the carbon anode forming CO_2 gas. At the cathode, elemental aluminum deposits as a molten pool in the bottom of the reduction cell.



A considerable amount of excess carbon consumption can occur due to characteristics of the reduction cell, the carbon anode, or the calcined petroleum coke used to make the anode [Hardin and Gehlbach, 1992]. As you can see from the equations above, ideal theoretical carbon consumption (weight of carbon consumed / weight of aluminum produced) from the stoichiometry of the ideal reaction is 0.334. Most modern smelters are now able to operate in the range of 0.38 to 0.40 carbon

consumption with electrical current efficiencies above 95%. Some of the side reactions that lead to excess carbon consumption are listed in Equations 2 & 3 that follow. The first describes air reactivity of the carbon anode with the atmosphere at the top (exposed portion) of the anode. The second shows the CO₂ reaction that can occur at the bottom of the anode. In this case, the CO₂ produced further reacts to consume additional carbon in order to form CO. Some physical and chemical properties of the calcined coke (described in the previous section) can directly affect one or both the air and CO₂ reactivity of the coke and subsequently the carbon anode.



Carbon Anodes. Aluminum reduction cells in today's smelters use two types of carbon anodes, prebaked and Soderberg. Carbon anodes should be dense, strong, electrically conductive, and of high carbon purity. Anode properties depend on the quality of the calcined petroleum coke, the quality of the pitch that is used to bind the coke, and the processing steps in preparing the anodes. Uniformity of the coke is important to permit suitable anode fabrication and processing. Deficiencies in anode quality can affect overall reduction cell performance, electrical current efficiency, and aluminum metal purity. These factors directly affect the cost of aluminum production for the smelter [Hardin and Gehlbach, 1992].

Prebaked. Prebaked anodes are made from CPC crushed and screened to obtain specific particle sizes. Used anode pieces or "butts" are recycled in the process to make most of the coarse fraction. The particle fractions are then mixed in proper proportions with a pitch binder (usually coal-tar based), formed into a body using a press or a vibrating form, and baked slowly to a high temperature (~1200°C) in an anode baking furnace ("ring furnace") to carbonize the pitch and drive off volatiles. This process is depicted in Figure 10. Several prebaked anodes are used in a single prebake reduction cell. A cross-sectional view of a prebake reduction cell is shown in Figure 11. Several reduction cells are linked together with electrical bus bars to form large potlines [Hardin and Gehlbach, 1992].

The flowchart illustrates the anode production process. It begins with 'Coke & Butts' being fed into a 'Crusher'. The output of the crusher goes to a 'Ball Mill'. From the 'Ball Mill', the material is sent to a 'Pitch' container. The 'Pitch' container feeds into a 'Mixer'. The 'Mixer' output goes to a 'Vibrator'. The 'Vibrator' output goes to a 'Press'. The 'Press' output goes to a 'Baking Furnace'. The 'Baking Furnace' output goes to a 'Baked Anode Ready for Pot'. The 'Baking Furnace' also feeds back into the 'Crusher' via a 'Screener/Classifier'. The 'Screener/Classifier' has three outputs: 'COARSE', 'MEDIUM', and 'FINE'. The 'COARSE' output goes to the 'Crusher'. The 'MEDIUM' output goes to the 'Crusher'. The 'FINE' output goes to the 'Crusher'. The 'Crusher' also feeds back into the 'Screener/Classifier' via a 'Pitch' container. The 'Crusher' also feeds back into the 'Screener/Classifier' via a 'Pitch' container. The 'Crusher' also feeds back into the 'Screener/Classifier' via a 'Pitch' container.

Alumina

Air cylinder

Anode current supply

Fume collection

Clamps

Anode Rods

Crust breaker

Removable cell covers

COLLECTOR BAR

Alumina crust

Frozen ledge

Carbon anode

Cryolite

MOLTEN ALUMINUM

CATHODE CARBON LINING

Refractory Lining

Floor

Cathode current

$$2\text{Al}_2\text{O}_3 + 3\text{C} + \text{Power} \rightarrow 4\text{Al} + 3\text{CO}_2 + \text{Heat}$$

~2 KG ~0.4 KG ~14.3 KWH 1 KG. 950-970°C

FIGURE 11 CROSS-SECTIONAL VIEW OF A PREBAKE REDUCTION CELL

20

pieces or “butts” are then re-used as a coarse component of the green anode mix. The rods/stubs are also cleaned and returned to be rejoined with newly baked anodes ready for service. If an anode is used too long, the connecting pin may become exposed in the bath, and the pin materials (mostly iron and copper) could contaminate the aluminum.

Soderberg. Soderberg cells use one massive anode in each reduction cell. These anodes are self-baking from the heat of the reduction cell and are continuously replenished by adding a coke-pitch mixture (paste or briquettes) to the top of the anodes. Some Soderberg anodes have vertical anode stubs or rods that carry the electricity through the anode. As the anode is consumed, stubs nearing the bath level are pulled and new ones are placed near the top of the anode. An illustration of a Vertical Stub Soderberg (VSS) cell is shown in Figure 12. Other Soderberg cells are operated in a similar fashion but have horizontal anode stubs. These are called Horizontal Stub Soderberg (HSS) cells.

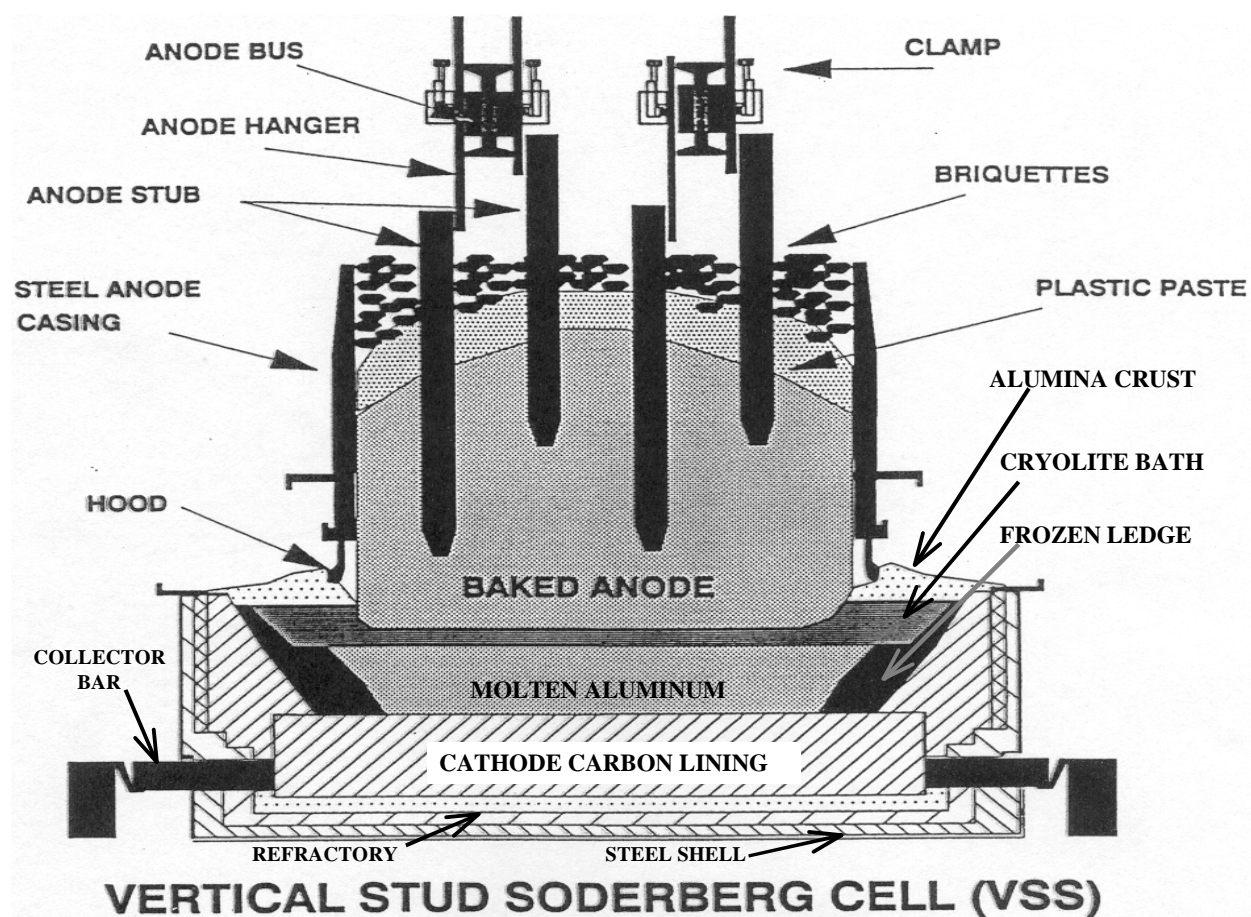


FIGURE 12.

The disadvantage of the Soderberg reduction cells is that the pitch fumes and dust in the potrooms tend to be highly concentrated making working conditions in these types of smelters

very undesirable. Employee safety concerns have led some aluminum companies to replace Soderberg pots with prebake pots and almost all future grassroots smelters will use prebake technology. Another drawback is that anode problems in a cell can be very difficult to remedy. In a prebake pot, troublesome anodes can be identified and replaced. These and other problems also lead to higher carbon consumption in smelters using Soderberg pots than smelters with prebake pots.

Graphite Electrode Manufacturing

Needle Coke / Special Coking. Anisotropic (needle) coke is required for graphite electrode manufacturing. Needle coke is formed from the mesophase or liquid crystalline type coke. Coking of needle coke is similar to growing crystals in that the lower the temperature, the larger the needles and the lower the CTE. A special coker feedstock high in aromatic hydrocarbons, decant oil from the bottoms of fluid catalytic cracking product, is normally de-ashed using special chemicals to enhance the settling of the catalyst fines or by filtering the decant oil through a series of catalyst filters. The decant oil is then usually hydrosulfurized to less than 0.7% sulfur in order to meet the sulfur specifications required in the green needle coke. Higher than typical coking temperatures, pressure, and recycle rates are used to produce a maximum amount of needle coke that is very low in volatile matter.

Needle Coke / Special Calcining. It is difficult to calcine needle coke to obtain the best properties. The coke mesophase has a tendency to revert to a liquid during rapid heating. When the volatile matter starts to evolve during calcination, bloating of the structure occurs leaving a low-density coke with a higher CTE. Volatile matter in the coke can also cause some of the particles to fuse together which also causes the CTE to increase. Some needle coke producers partially devolatilize (preheat) the coke before calcining to prevent bloating and to keep a low CTE. Graphite electrode manufacturers now demand that the needle coke CTE be below 2×10^{-7} cm/cm/°C.

The usual specification on RD for needle coke is 2.13 g/cc. Rotary kiln calciners are normally used to calcine needle coke because rotary hearths tend to produce too many fines (minus 1 mm) during calcination. In calcined needle coke, coarse particles (+6 mm) are desired. Greater than 0.78 g/cc 4 to 6 mesh bulk density is also required. Low ash content, < 0.3 wt% ash, is required since any ash would leave a void in the structure when graphitized. Even with all the property specifications, an electrode manufacturer will not accept calcined needle coke for production until they have actually run a trial lot through the plant and trials on an electric arc furnace. Obtaining good needle coke is still a “black art” for excellent graphite electrodes [Ellis and Paul, 1998].

Lengthwise Graphitization. Low (<0.6-0.7 wt%) sulfur calcined needle coke is necessary for making electrodes due to the rapid heating in lengthwise graphitization to 2900°C. The evolution of too much sulfur can cause the electrode to crack open (puff) similar to an over-cooked hot dog. Needle coke is required to meet the low CTE requirement of the graphite electrode in the lengthwise direction. Low CTE allows the electrode to operate with a high temperature gradient without spalling the hot tip. When an electrode arcs with the steel in an electric arc-furnace, the thermal gradient is over 2000°C per centimeter.

Most graphite electrode plants want a needle coke with low variability so that they can set up the optimum coal-tar pitch level for making the electrode paste, extruding, and baking to produce a good electrode. The electrode is manufactured using sized calcined needle coke with around 27% coal-tar pitch. The electrode paste is then extruded so that the needles in the coke align in the direction of extrusion. Green electrodes are baked and impregnated several times with petroleum pitch before lengthwise graphitization [Ellis and Paul, 1998].

Use of Graphite Electrodes – Arc Furnace Steel Production. The most popular electrode is the 24 inch (60 cm), with a demand for larger than 30 inch (76 cm) for single electrode DC furnaces. The principal property that an electric arc furnace steel mill wants in graphite electrodes is low graphite use (electrode consumption) per ton of steel produced. In single electrode DC furnaces, graphite use per ton of steel is below 2 kg. With better practices and use of foamy slag, AC furnaces (using three electrodes due to three-phase electric power) have approached this level [Ellis and Paul, 1998].

Specialty Graphite Industry

Graphite Moldstocks. Very large pieces of graphite are used for casting large items such as (steel) railcar wheels. To make the graphite, very fine-grained calcined coke with high density and high CTE is needed. Calcined isotropic (shot or near-shot type) coke is preferred. The molds are usually used upside down with the molten steel flowing up into the molds.

Semi-Graphite Electrodes. Semi-graphite electrodes are produced from calcined sponge coke for specialty electric furnace uses such as in manufacturing phosphorus or titanium dioxide (from rutile/ilmenite ore preparation - sulfate process). Low (usually <1%) sulfur calcined coke mixed with pitch is extruded into electrodes and then partially graphitized.

Titanium Dioxide Production

Calcined petroleum coke is used in the production of titanium dioxide (in the chloride process). A flow diagram of the titanium dioxide chloride process is shown in Figure 13. The calcined coke must be sized (usually to < 5 mm) for use in the fluidized chlorinator reactor (see Figure 14) where the coke reduces the titanium dioxide from the ore (forming CO and CO₂) and furnishes heat for the chlorination of the titanium to titanium tetrachloride. Further processing by oxidizing the titanium tetrachloride results in pure titanium dioxide product in a powdered form. Chlorine is recycled and returned to the chlorinator. Finished titanium dioxide is commonly used as a brilliant white pigment for paint, paper, plastics, ceramics, textiles, rubber, and inks, and is also used in pharmaceuticals [Pace Consultants 1990].

For this application, low moisture ($<0.3\%$), low hydrogen ($<0.2\%$), hard calcined coke is desired with a minimum amount of fines (usually $< 5\%$ minus 60 mesh). Any moisture or hydrogen would form hydrochloric acid in the chlorinator, and coke fines have a tendency to be blown out of the process. The metals in the coke are not as critical as in aluminum anodes, but low ash is desired since it becomes a waste removal problem forming slag in the chlorinator. Although typical sulfur values usually vary from 2.5-3.5 wt%, some customers prefer lower sulfur coke due to environmental emission limitations.

Chemical Processing: Carbon Monoxide for Polycarbonate Plastics Production

Sized calcined petroleum coke with low hydrogen content is used in a gasification process (in Stauffer-type CO Generators) to make carbon monoxide. A simplified process flow is presented in Figure 15. Further synthesis produces phosgene gas used for the production of high strength polycarbonate plastics. Low hydrogen is needed to prevent the formation of hydrochloric acid during the chlorinating of the carbon monoxide. Sizing is critical in some applications to transport the coke via pneumatic systems.

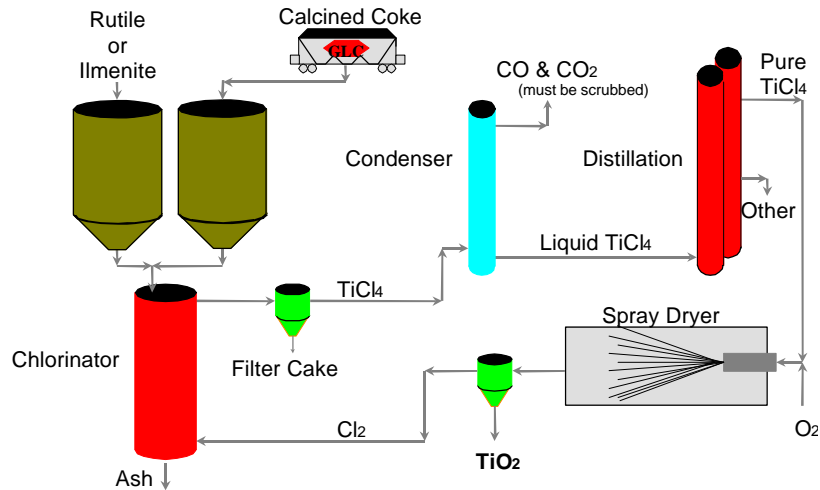


Figure 13. TiO₂ Process Flow Diagram.

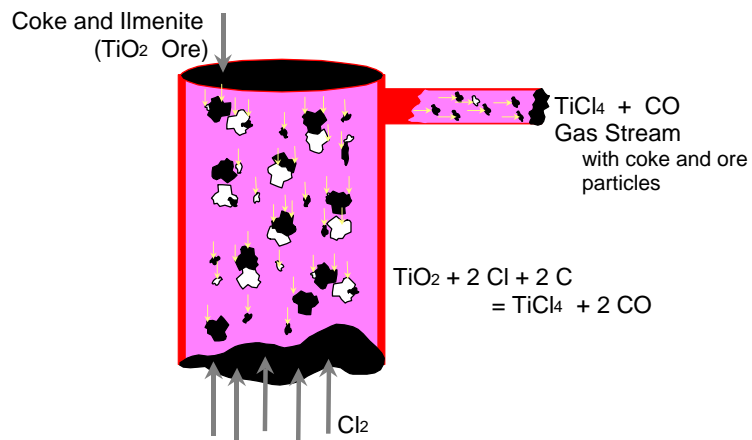


Figure 14. TiO₂ Chlorinator Reactor.

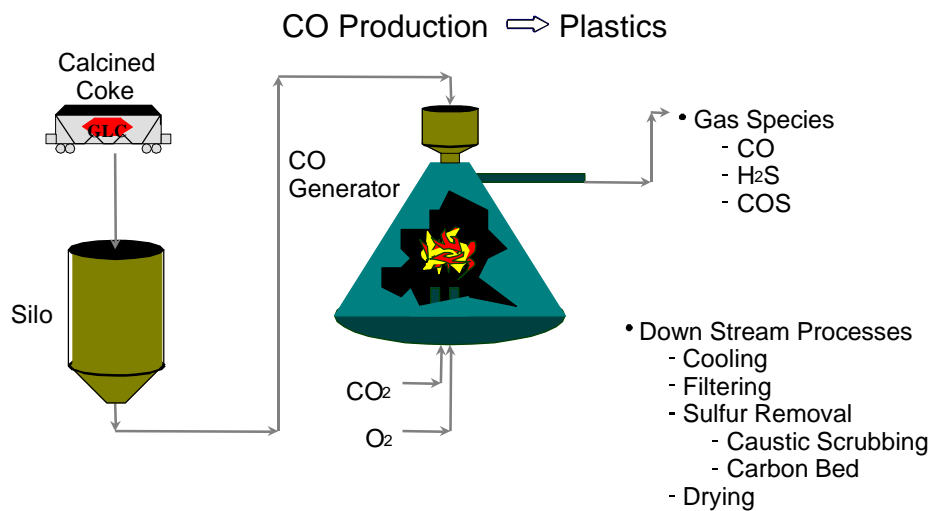


Figure 15. CO Production Process Flow Diagram.

Steel Production

Figures 16-18 illustrate the use of charge carbon and injector carbon in the steel industry.

“Carbon Raiser” / Recarburizer – Charge Carbon. Several different types of calcined coke are used to increase the carbon level in steel. During the purification and melting of steel (scrap iron), oxygen is injected along with lime to take out impurities and form a foamy slag on top of the molten steel. The foamy slag helps insulate the molten steel by reducing surface heat losses. The oxygen burns the charge carbon producing additional heat in the melt. Initial charge coke added with the scrap steel must have high carbon purity. There can be a little sulfur (usually 1-3%) in the calcined coke since lime that is injected later will remove sulfur. As the steel is further refined, lower and lower sulfur content calcined coke must be used as the “carbon raiser” with extremely low (<0.1 wt%) sulfur carbon for the ladle additions. Sulfur is undesirable in steel since it causes brittleness.

Injector Carbon. Injector carbon is normally sized low sulfur calcined coke. Sizing (usually to < 5 mm) is necessary to prevent plugging in the injection system. Injection is used to put the carbon into the melted steel below the foamy slag (floats on top of the molten steel). The amount of sulfur is critical, and the amount of nitrogen in the coke can cause problems with heat treatment of cast steel parts. Very high temperature calcining can decrease the nitrogen content of the CPC.

Ladle Additives. Ladle additives require carbon material with very low sulfur (<0.1 wt%) and low nitrogen contents. Low hydrogen in the carbon is also desired to prevent hydrogen embrittlement. Graphite scraps or crushed old graphite electrodes are most commonly used. Coke made from ethylene tar (obtained from ethylene cracking) is low enough in sulfur and nitrogen to be calcined for use as ladle additives. Superior Graphite Company has a proprietary process in which calcined petroleum coke is electrically graphitized through a continuous particle thermal desulfurization process. This reduces the sulfur, nitrogen, and metals to extremely low levels to make a product that is an excellent ladle additive.

Blast Furnace Linings. Another use for low sulfur calcined coke is in making special refractory bricks for blast furnace linings. Bricks are pressed using calcined coke with a pitch-type binder and baked in a special pit-type furnace. The calcined coke used must be low in sulfur to prevent sulfur contamination of the steel.

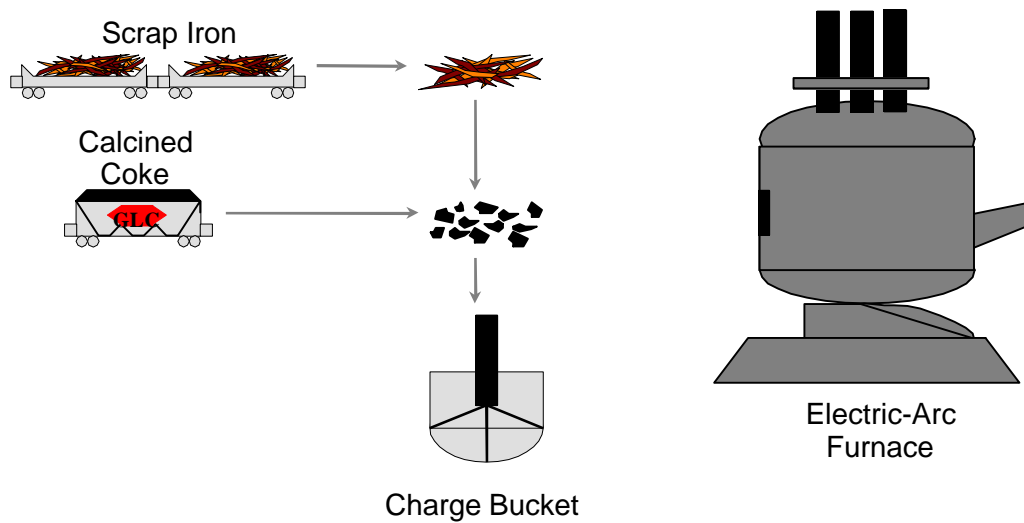


Figure 16. Recarburizer for Steel: Charge Carbon.

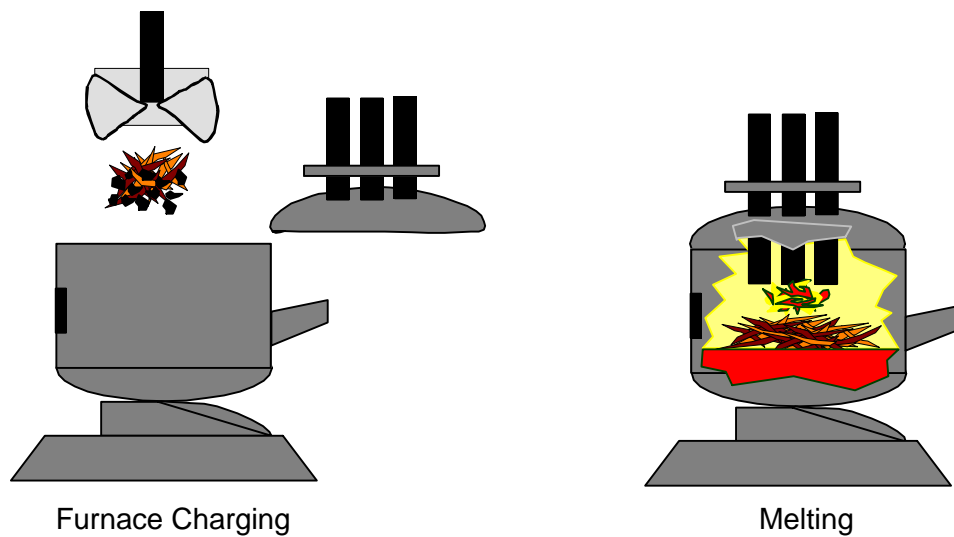


Figure 17. Recarburizer for Steel: Charge Carbon.

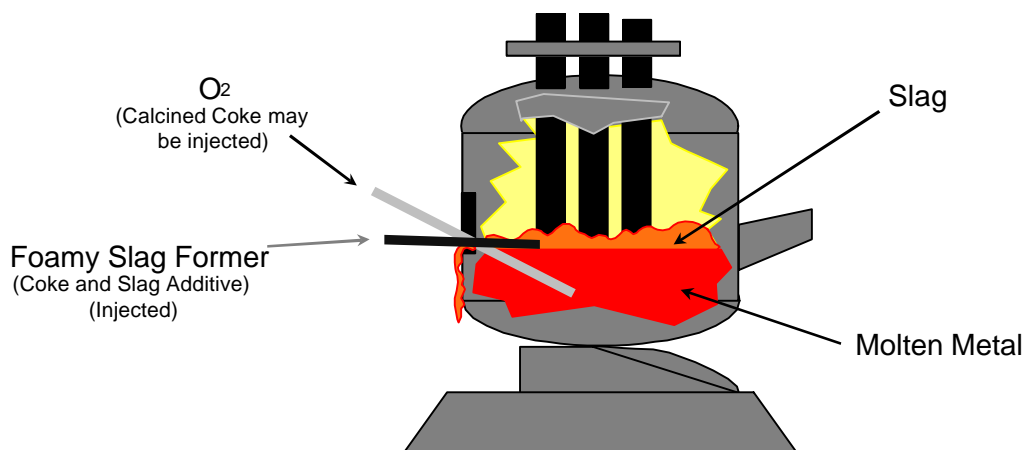


Figure 18. Recarburizer for Steel: Foamy Slag Forming.

Fluid Coke Calcining / Uses of Calcined Fluid Coke or Sized Sponge/Shot Coke

A calcining plant was built in 1959 at Purvis, Mississippi for calcining fluid coke. A fluid coker at an adjacent refinery supplied the raw material. Size and properties of fluid coke are very poor in comparison to coke from delayed cokers. The primary markets for calcined fluid coke include cathodic protection of pipelines and packing media for anode baking furnaces.

Cathodic Protection. The preferred material for cathodic protection of pipelines is calcined fluid coke with good electrical conductivity. Graphite electrodes are used to electrically connect the pipeline to the earth as an anode. Calcined coke is poured around the graphite electrode to prevent electrical erosion of the expensive graphite and to increase the physical total contact with the earth. Rectifiers are used to impress a voltage on the pipeline to prevent corrosion. The coke must have good electrical conductivity and be sized so that it can be easily poured into holes around the graphite electrode. The material should be low in dust to prevent excess losses when handling. It must also be easily water-wetted for ease in slurry pumping. Some operations slurry the coke with water and pump the slurry into the space around the electrode.

Anode Baking Furnace Packing Media. Although crushed and sized anode grade CPC is the preferred packing media for most anode baking furnaces, some calcined fluid coke is used in baking furnaces designed with tight tolerances between the flue walls and the anodes. Depending on the baking furnace design, other material such as crushed and sized calcined shot or sponge coke may be used.

ACKNOWLEDGEMENT

We would like to thank the following people from Great Lakes Carbon for information used in this paper:

Larry J. Pinkston	Director of Corporate Engineering
Frank Welter	Former Plant Manager – Port Arthur, TX
Carl Peters	Former Corporate Patent Attorney

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