

# 1. HALL-HÉROULT CELL CARBON ANODES

Papers on carbon anodes have been published in every *Light Metals* volume. Many of the early papers published are still relevant today and a review of the titles show reappearance of similar issues over the 40 years of publication. The papers selected do have a historical perspective but also reflect today's industry and issues. There is a stronger focus on prebaked anode production and performance over Söderberg paste, and there are a number of papers relevant to current issues with coke quality and supply. In other areas such as thermal shock of anodes, the number of papers reduced after the mid 1990s, suggesting the 1994 paper by Meier et al. titled "Thermal Shock of Anodes – A Solved Problem?" was accurate in predicting that a solution to the problem could be identified.

The anode papers are separated into subsections related to raw materials, anode production, and anode performance. The objective is to allow readers to delve deeply into a specific topic and find like papers together. Where possible, review or general papers related to the topic are included first in each section, followed by papers that are more detailed or are related to a specific topic. The papers should be read in conjunction with the recommended reading list at the end of the section.

**CALCINED COKE FROM CRUDE OIL TO CUSTOMER SILO**

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**ABSTRACT**

The quality of calcined petroleum coke used in primary aluminum production is affected by each of the refining and calcining processes including choice of crude, many of the initial refinery processing steps, coking, calcining as well as the handling systems between the refinery, calciner and final customer. This paper will discuss how each of these processes affects the final quality of the resulting calcined coke to give insight as to how refining economics will be affecting calcined coke quality in the future.

**INTRODUCTION**

Calcined coke quality is a complex, multi-variable topic. There have been many attempts to predict calcined coke quality in terms of metal content, sulfur content, porosity, structure etc. Many different equations have been used to predict how a coke will perform in an anode with respect to air burn, CO<sub>2</sub> reactivity, CTE etc. The need to use many different equations to predict the same anode performance property (1) suggests there are probably additional coke properties or anode fabrication variables that are not constant in the cokes or anodes being studied. Consequently, this paper will address calcined coke quality from the refining and calcining viewpoint. There have been a significant number of papers defining the effect of calcining conditions on calcined coke quality (2, 3, 4) but limited literature information on the effect crude quality has on calcined coke quality (5 & 6). This is unfortunate since crude oil composition is probably the largest factor affecting a calcined coke's potential structure, its sulfur content, and some metal impurities.

There is no one property that can be singled out to identify a good quality calcined coke. Instead there are many properties taken together that describes the quality of calcined coke. How these properties are achieved is also a trade off. That is, improving one calcined coke property in a desired direction often reduces the

quality of another property. For example, reducing the resid cut point or increasing the coker recycle ratio reduces the coke's vanadium and nickel content but the resulting calcined coke's particle strength and sizing can be reduced. Typically, calcined coke quality is not a major factor in refinery crude selection and design.

**Calcined Coke Specifications & Controlling Production Factors**

<u>Specification</u>	<u>Major and minor factors</u>
Real Density	Calcination temperature and time.
Bulk & Apparent Density	Crude, Volatile content of green coke and calcination heat up rate.
Impurities: Sulfur/Nickel/Vanadium	Crude, vacuum cut point, and coking conditions
Iron	Crude, crude desalting, coke handling systems
Silicon	Coke handling and storage
Calcium	Water quality (coking, calciner cooling, & other water systems)
Sodium	Water quality (coking, calciner cooling, & other water systems), and crude desalting
Sizing	Crude, vacuum cut point, coking conditions, handling systems and segregation
Air Reactivity	Water quality (coking and cooling etc.), metal content, calcining conditions
CO <sub>2</sub> Reactivity	Crude sulfur content, surface contaminants such as sodium.

The refinery's primary concern is to process the most cost-effective available crude that matches refinery design capability and maximizes the value of the products produced. In general, this equates to maximizing liquid yield. This paper will address how the following operational choices affect various calcined coke quality parameters and how refinery economics will affect calcined coke quality.

**PETROLEUM CRUDE OIL QUALITY** (coke's sulfur, nickel, vanadium, iron, bulk density, CO<sub>2</sub> Reactivity, Air Reactivity, and sizing) The quality of the resulting calcined coke starts with the choice of crude oil or crude oil blend being refined.

Given a choice, most anode manufacturers would choose to have a zero ash, zero metals, high bulk density, medium 2% to 2.5% sulfur coke consisting of a consistent supply of over 30% +4 mesh calcined coke supply to make anodes. This combination of properties is not possible because many of these properties come from conflicting crude properties. In order to have a high bulk density coke, the crude needs to contain a significant amount of asphaltenes. Asphaltenes are complex polyaromatic compounds which contain essentially all the nickel, vanadium and iron found in the crude oil. However different crudes can have asphaltenes with different levels of metals associated with the asphaltenes. This can be seen in the data presented in Table 1 by dividing the total nickel and vanadium content by the asphaltene content. There is a general relationship that calcined coke made from higher asphaltene containing resid (also higher vanadium and nickel) will also have higher bulk density.

A coker feed stock that has essentially no asphaltenes and no vanadium, nickel or iron is clarified oil that is obtained from a fluid catalytic cracker. Coke made from this highly aromatic feed stock makes a needle coke which is used to make electrodes for the electric steel industry. Although calcined needle coke has many desirable properties for aluminum anodes such as low reactivity and very low thermal expansion, it also has very undesirable properties such as, low bulk density, high porosity, very poor particle strength and size. Anodes made from this coke would require unusually high pitch content and result in very low-density anodes with poor structural strength.

In general, as the asphaltene content of crudes increase, the resulting coke's bulk density, particle strength as well as its vanadium and nickel content increases. Crudes that have too many asphaltenes tend to make shot coke and contain very high levels of nickel and vanadium. A paper by Ellis and Bacha on shot coke (5) suggested that shot coke formed when pentane insolubles (asphaltenes) of the coker feed are above 13.5%. The author's experience is that higher asphaltene content increases shot coke production but the chemistry and molecular weight of the other resid components also affects shot coke production. If the other resid components are highly aromatic and the asphaltenes are medium molecular weight, significantly higher

asphaltene containing resids can be coked without shot coke production. For example, Alaskan North Slope resid with asphaltenes above 16% makes a good high bulk density coke.

Table 1 lists some crude, resid assay data and predicted green coke quality data from an ARCO coker model. The green coke quality is calculated for a refinery sending relatively deep cut resid to a coker with a low recycle ratio. These are the conditions most refineries would choose if they only wanted to maximize liquid yield with little concern for green coke quality.

The crudes listed in Table 1 are chosen from different geographical parts of the world. Crudes are often characterized by where they are produced. Crudes from various locations in the world tend to have similar quality. For example, crudes from Venezuela and Mexico are heavy, highly aromatic, having high sulfur and high asphaltene content. Crudes from this area produce mostly isotropic very dense and often shot coke. Crudes from the Middle East tend to be slightly less heavy but contain significant sulfur and metal levels. Whereas crudes from Indonesia are very waxy (paraffinic) with very low sulfur and metals content. These crudes produce low metal and sulfur calcined coke but with low bulk density and poor sizing properties. Crudes from North Africa, West Africa and the North Sea have relatively low sulfur and metal contents as well as low asphaltene content. These crudes make low metal and sulfur cokes but with lower bulk density.

**Table 1**  
Predicting Green Coke Metal and Sulfur Content from Crude and Resid Data

Crude/Location Name	Venezuela Hamaca	Mexico Maya	Saudi Arabia Arabian Med	USA ANS	Nigeria Forcados	North Sea Brent	China Liahua	Indonesia Minas
API	8.6	21.5	28.6	28.9	28.1	37.5	39.6	34.0
MCC, wt%	15	10	6	4	1	2	5	3
Sulfur, wt%	3.9	3.4	2.8	1.1	0.2	0.3	0.6	0.1
Metals, ppm								
V	302	237	19	19	1	3	1	1
Ni	85	38	9	9	4	1	5	9
<b>Resid</b>	<b>Resid Cutpt: 1000F</b>	<b>Coke Drum Temp: 840 F</b>	<b>Pressure: 30 psig</b>	<b>TPR: 1.12</b>				
Vol% of Crude	54	35	25	22	7	13	35	25
API	0.0	1.5	5.1	8.1	13.8	12.4	12.6	16.6
USOP K	11.5	11.8	11.5	11.7	12.1	11.8	12.3	12.4
MCC, wt%	27	29	25	20	13	14	14	10
Asphaltenes, wt%								
Pentane Insolubles	23	25	18	16	4	2	6	22*
Sulfur, wt%	4.5	5.7	5.8	2.6	0.5	1.1	0.2	
Metals, ppm								
V	557	680	83	95	7	20	2	3
Ni	157	110	39	42	52	5	15	35
<b>Green Coke</b>								
Coke Yield, wt%	40	38	31	25	24	23	23	15
Wt% Sulfur	4.6	6.2	7.8	3.2	0.8	1.9	0.4	0.4
ppm V	1,377	1,796	272	385	29	88	7	<10
ppm Ni	388	290	128	167	216	20	64	220

\*The high saturate content of this crude has non-asphaltenes being reported as asphaltenes due to analytical test conditions.

Bulk Density Higher Lower

The green coke data in the table indicates the very high metal content (vanadium 1377 ppm to 1800 ppm) of coke obtained from Venezuelan and Mexican crudes. The predicted green coke quality for Venezuelan crude was verified in a study commissioned by the state owned Venezuelan oil company made by R&D Carbon (7).

The choice of crudes processed in a refinery is strongly affected by crude logistics, refinery metallurgy and refinery design, and is normally independent of coke quality considerations. That is, refineries are normally designed to process a given crude type. The choice of crudes to feed a refinery is based on the most cost-effective crude available during refinery start up. One of the first considerations is the location of crude relative to the refinery. Crudes processed in Europe often come from North Africa, West Africa and the North Sea. These relatively sweet crudes (less than 1 % sulfur) are processed in European refineries and Southeast Asia refineries with metallurgical capabilities of processing these relatively easy to refine crudes. Refineries in Texas and Louisiana process crudes from Texas, Oklahoma and Louisiana and other fields around the Gulf of Mexico. Since most of these crudes are more sour (higher sulfur content) than the African crudes, most of the refineries in the Gulf States have a more sophisticated metallurgy capability of processing these crudes. The waxy crudes from Indonesia which are refined in Indonesia and Southeast Asia produce a high volatile content green coke which produces a coke with poorer sizing and lower bulk density.

**REFINING PROCESS**

The typical coker refinery flow scheme is depicted below:

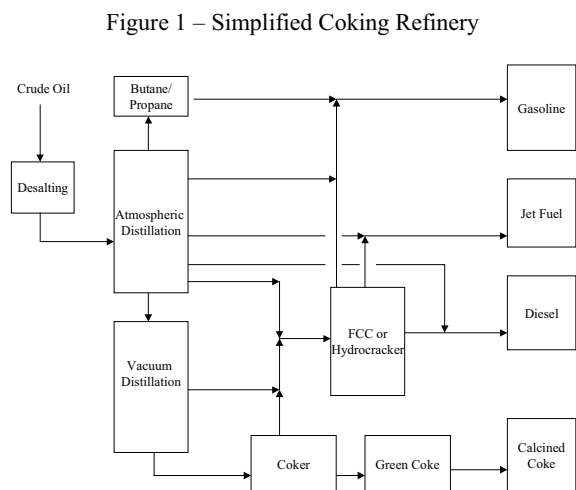


Figure 1 – Simplified Coking Refinery

**Desalting**

The first refining process that affects the quality of calcined coke is the desalting of the crude oil. Crude oil coming from the ground is a mixture of petroleum hydrocarbons, salt water and suspended solids. Before distilling the petroleum hydrocarbons, the salt, water and suspended solids need to be separated from the oil. This is done in a desalter where the crude oil is mixed with fresh water to wash out the salt content (mostly sodium chloride). The efficiency of this desalting step depends on the crude quality. Some crudes contain surfactants which help form an emulsion that is difficult to break. However, this first step of the refining process is needed to remove the sodium and chlorides associated with the crude oil. Chloride is a major corrosion catalyst and if not removed will significantly corrode the pipes and refinery units the oil is processed through. Low sodium content coker feed results in smoother coker operation by reducing the coker heater fouling (8). Although desalting the crude is done to protect the refinery piping and reduce coker tube fouling, removing the chlorides

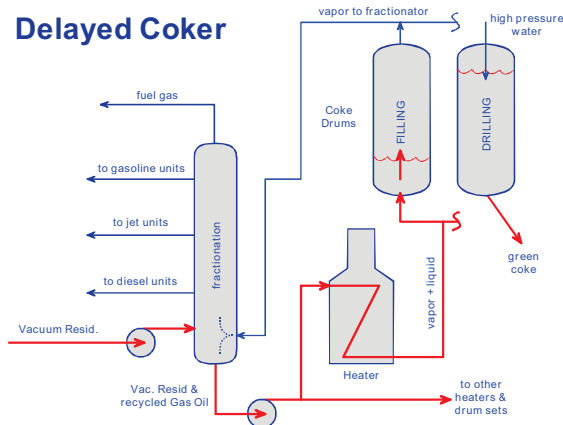
reduces the iron content that finds its way into the coker feed and eventually the coke.

**DISTILLATION**

After desalting the crude oil, the petroleum hydrocarbons are separated by distillation. Distillation is the refiner’s most common unit operation. Coker feedstock is produced in refineries by distillation of crude oil. The basic principle of distillation is to separate a mixture of liquid components by their different boiling points. Crude oil is a mixture of hydrocarbon compounds which range in boiling points from 0-800+°C. Crude oil in the modern refinery is distilled under atmospheric pressure, followed by distillation under vacuum. These processes yield finished and intermediate products that are sent to catalytic units to produce high-octane gasoline blending components, jet fuel, diesel fuel, and liquefied petroleum gas. The heaviest product generated in vacuum distillation is the coker feedstock (or resid).

**COKER OPERATION**

Figure 2 – Schematic of Coker Operation



A coker usually comprises one distillation tower (often referred to as a "fractionation tower"), one heater and 2, or more coking drums. The primary feed to the coker is the resid from the distillation units. Some refineries will include ancillary streams in the coker feed. They may include thermal tars (from thermal crackers or visbreakers), decant oils (from fluid catalytic crackers) or aromatic discharges (from lubricating oil processing). Warm resid (coker feed) is fed to the fractionation tower, then pumped to a coker heater where it is heated to approximately 500° C before entering the coking drum. At this temperature, cracking and polymerization reactions take place. Great care is taken to insure coke is not deposited in the heater tubes or in the transfer piping leading from the heater to the coking drum. Refiners minimize coking in these areas by running high velocities in the furnace tubes, and minimizing the distance between the coker heater and the coke drums. A common industry practice is to inject high-pressure steam into the heater tubes to control velocity. When the hot resid enters the large diameter coke drum, the velocity is drastically reduced.

Controlling the velocity of the process to insure coking in the drum and delay coking in the heater tubes and transfer piping has given this process its name: "delayed coker".

Inside the coke drum, a complex mixture of cracking and polymerization reactions take place. The overall process is endothermic (absorbs heat), but exothermic (generates heat) reactions also take place. The irreversible transition of liquid hydrocarbons into solid coke is not fully understood, however, an intermediate phase termed "mesophase" has been identified. A similar phase transformation takes place for the binder during anode baking.

The vaporized cracked products from the reaction in the drum flow overhead and are returned to the fractionation tower. From the fractionation tower, gas and intermediate product streams are separated and routed to catalytic units. Virtually all the metals in the coker feed end up in the coke while the sulfur is distributed throughout the liquid products and coke.

Delayed coking is a semi-batch process. After a drum has been filled with coke, it is cooled down by steam, followed by water. The top and bottom heads of the drum are then removed and a drilling process commences. First, a pilot hole is drilled in the center of the drum from top to bottom followed by cutting of the coke by high pressure (about 3000 psi) water jets. This cutting starts at the top, and as coke breaks loose and falls down through the pilot hole onto a concrete pad below.

After the drum is emptied, the heads are put back on and hot hydrocarbons are passed through to preheat the drum prior to the introduction of resid. While all this is taking place, another drum is being filled.

### **EFFECT OF COKER OPERATION PROCESS VARIABLES ON CALCINED COKE**

#### Resid Cut Point (coke vanadium, nickel & sulfur, bulk density)

The resid (coker feed) cut point has a significant effect on the sulfur and metal content of the resulting green coke. If the resid is cut deeper the asphaltene content will increase. As discussed in the crude section, this will increase the coke's bulk density and metals content. Choosing a lower resid cut point results in more heavy gas oils being sent to the coker. Since the heavy gas oils do not contain vanadium or nickel, the coke made from these gas oils will reduce the coke's overall vanadium and nickel content.

The resid cut point can have an effect on the coke's sulfur content. For crudes that are very low in sulfur content such as Indonesian and North Sea crudes, the resid cut point has very little effect on the sulfur content of coke. For crudes that are higher in sulfur content, the sulfur content usually increases in the heavier cuts. For these more sour crudes, increasing the resid cut point will increase the sulfur content of the resulting coke.

#### Recycle Ratio (coke vanadium, nickel, and particle strength)

Recycle ratio is the volume flow ratio between the heater feed and the vacuum resid feed. The heaviest cracked hydrocarbons returned to the coker fractionation tower are "recycled" to the coke drum, thus making the volume flow through the coking drum higher than the coker vacuum resid alone. At recycle ratio of one, no recycle takes place ("once-through operation"). Some refer to recycle ratio as "combined feed ratio" (CFR), or "throughput ratio" (TPR).

As the recycle ratio is increased, the coke yield is increased which reduces the coke's nickel and vanadium content and increases the anisotropy (ordering) for the calcined coke. As indicated earlier, coke made from high asphaltene content resid can be isotropic. As additional heavy aromatic gas oil is recycled to the coker, the green coke will yield a more anisotropic calcined coke. Increasing the recycle ratio also can reduce the particle strength of the resulting coke if the coking temperature is not increased appropriately.

The refinery's choice of resid cut point and recycle ratio depends on the type of units the refinery uses to process heavy gas oils. Some units such as fluid catalytic crackers can economically process very heavy gas oils but hydrocrackers can not due to components from the heaviest gas oils poisoning the hydrocracker's catalyst. Varying a cokers resid cut point and recycle ratio to optimize the different heavy gas oil cracker units can increase or decrease a coke's vanadium or nickel content by 20% to 30%.

#### Coker Heater Outlet Temperature (Bulk Density, coke particle strength, Shot coke content)

Coking temperature will affect the resulting calcined coke's physical properties such as porosity, bulk density, sizing and particle strength. High temperature reduces green coke VM (volatile matter) content and HGI. This results in a calcined coke with higher VBD and lower porosity. If the coke temperature is too high, it becomes difficult to remove the coke from the drum and could increase the shot coke content. One method to reduce the shot coke content is to reduce the coker heater outlet several degrees. If the coking temperature is too low, the coke comes out of the drum as a tarry goo which requires no drilling.

At the 1992 Australasian Smelting Workshop a correlation between coker drum temperature and green coke volatile content was presented (ref. 14 page 184). This correlation was obtained from pilot plant coker studies. Although this correlation is valuable for understanding what affects green coke volatile content, using this approach in commercial cokers is much more complicated. The inside drum temperature of commercial cokers is not monitored or controlled and will change due to other factors affecting coker operations. While the coker heater outlet temperature significantly affects the inside coke drum temperature other factors such as resid cut point, resid recycle ration, coker pressure etc. will also affect the inside drum temperature. Crude and resid composition also will affect the green coke volatile content since the chemistry of the resid will affect the ratio of exothermic and endothermic reactions occurring in the coke drum.

### Cycle Time (Particle strength, & VBD)

Cycle time is the time it takes to fill a coke drum. It typically ranges from 12 hours to 20 hours with most cokers making changes to reduce the cycle time.

More vacuum resid can be fed to the coker per unit time if the cycle time is reduced. This may be desirable if the refinery processes more crude or processes a crude that yields more coker feed. Reduction in cycle time is often utilized to maintain coker capacity when the coke yield is increased as a result of different crudes being processed or when intermediate components are added to the coker feed. As the cycle time is reduced, the average residence time of coke in the coke drum is reduced. This will generally increase the volatile matter of the green coke, reduce the VBD and particle strength of the calcined coke. This can be compensated for with an increase in the coking temperature.

Increasing the coker heater outlet temperature reduces the green coke's volatile content and improves the calcined coke's sizing. However by increasing the coke drum temperature, more of the heavy gas oils which could form coke is evaporated from the coke drum. These evaporated heavy gas oils don't form coke, which would dilute the coke's vanadium and nickel content. This is another example of using one process variable that improves one coke property but adversely affects another coke property.

When green coke is formed in a coke drum the coke at the bottom of the drum will have different properties than coke at the top of the drum. Since the coke at the bottom of the drum has been soaking at significantly high temperatures for several hours and coke at the top of the drum being at temperature for as little as one hour, it is easy to understand why the volatile content of the coke from the top of the drum is higher than coke at the bottom of the drum. Green coke with higher volatile content is less hard and typically smaller in particle size than the lower volatile content coke from the bottom of the drum. The higher VM green coke also has lower nickel and vanadium content than the larger sized lower VM green coke.

### Cooling cycle (coke surface contaminants, coke reactivity)

Cooling the coke in the coke drum is considered part of the cycle time. When one coke drum is being filled the other paired drum is being cooled and drilled. After cooling the coke in the coke drum with steam and then water, the green coke is drilled from the drum with high-pressure water. The quality of the green coke cooling water, coker drilling water and the water to cool the calcined coke after calcining can affect the surface chemistry of the green coke. Since significant quantities of water are evaporated in these processes, the metals (sodium, calcium, etc.) dissolved in the water coat the outside surface of the coke. The metals on the surface of the coke have been shown to increase the calcined coke's reactivity. Controlling the quality of the water that comes in contact with the green and calcined coke can reduce the calcined coke's reactivity (9 & 10).

### Drilling the coke out of the drum (coke size distribution)

The techniques used to drill the coke can affect the resulting calcined coke particle size. Since high pressure water is used to

drill the coke drum, minimizing the drilling time will reduce the amount of green coke fines generated. However, as the drilling time is reduced there is a greater chance of coke in the drum caving in and damaging the drill stem. A cave-in usually requires the drilling operation be restarted beginning with another pilot hole. Consequently to help obtain a good sized calcined coke, the coke drilling techniques need to minimize drilling time but with a safety margin to protect from coke drum cave-in occurring.

When the coke is drilled from the coke drum the particles range in size from significantly less than one centimeter to one cubic meter. Before the coke can be calcined the very large pieces need to be crushed to a more manageable size for handling and processing. Typically the green coke is crushed to less than ten centimeters.

## **GREEN COKE HANDLING/STORAGE/SCREENING SYSTEM**

How the green coke is stored and transported affects the silicon content and sizing of the calcined coke. Moving green coke with a completely covered conveyor system to a covered barn to dewater the coke and then conveying the dried green coke to the calciner by another conveyor system will protect the coke from being contaminated with dirt (silicon, aluminum, etc.). Most refineries and calciners do not have the luxury of such a dedicated system and rely on storing the green coke on asphalt pads and moving the green coke by front-end loaders. This method of handling will result in calcined coke with higher silicon content.

Being able to store the green coke in a storage barn reduces the moisture content and the variability of the coke's moisture. Maintaining a more constant calcining temperature due to very low and consistent moisture content helps reduce the resulting calcined coke's real density standard deviation.

Screening the green coke feed to a calciner to eliminate the finer green coke can improve calcined coke sizing and reduce calcined coke porosity.

## **CALCINING**

Green petroleum coke is calcined to remove volatile hydrocarbons and to develop the crystal structure of the coke. Petroleum coke is not electrically conductive until its crystallinity is developed.

There are two types of calcining systems used to calcine green coke-Rotary Hearth and Rotary Kiln.

### Description of Marathon Wise (MW) Rotary Hearth Calcination

The MW furnace consists of a rotating, circular sloped hearth and a stationary roof from which a set of rabblers are suspended along a rabble pit from the periphery to the center. The rabblers clear the rotating hearth by approximately 5 cm. A water filled blade and trough seal provides airtight junction between the hearth and the roof section. Process air is introduced through wickets mounted on the sidewalls of the roof section and in the

roof. The process air is preheated, and the temperature and volume of the air can be adjusted independently.

Green coke is fed to the periphery of the hearth through a chute extending through the furnace roof. The chute extends to approximately 20 cm above the hearth thus leaving a row of approximately this height as the hearth rotates underneath it. After the coke has traveled one path along the periphery of the hearth, it is deflected inwards by the first rabble. The coke travels through concentric paths deflected towards the center of the hearth each time it hits a rabble. The last rabble pushes the coke into a soaking pit at the center of the hearth. This soaking pit is maintained full providing a seal between the calcined interior and the cooler.

A rabble on a discharge table underneath the soaking pit deflects the coke into a chute feeding the cooler. The coolers installed with rotary hearth furnaces are of the indirect type. The coke is maintained inside a drum while cooling is provided by water on the outside of the drum.

The hot gases are brought via a large duct to a steam boiler and a recuperator for preheat of the process air. Most calciners are equipped with sulfur scrubbers and some are also equipped with electrostatic precipitators for particulate control.

#### Description of Rotary Kiln Calcination

A rotary kiln consists of a rotating sloping tube calciner and direct water spray cooler. More modern installations also incorporate an after burner and an energy recovery system from the hot flue gases. The refractory lined kiln has a feed end (cold) and a discharge end where the burner is located. Green coke is fed through weigh feeders to the kiln's feed end and moved down the kiln counter current to the heat flow. Complete calcining of the coke takes place in the firing zone.

Process heat is supplied through a burner located at the discharge end of the kiln. It can be designed to burn gas, oil or solid fuel. To control the combustion of volatile material driven off from the green coke, secondary air is introduced through the firing hood. For optimum combustion of volatiles, tertiary air is introduced through the shell of the kiln. After complete calcination, the coke is discharged into a rotary cooler where it is quenched with direct water spray. The hot gases discharging at the feed end of the calciner consist of residual volatiles, carbon monoxide and coke particles carried out as dust. This gas is passed through an after burner where complete combustion takes place through introduction of excess air. In most kiln installations, the energy of this hot gas is recovered in a waste heat boiler. Steam from this boiler can be used for other processes, or for electricity generation through a turbine.

#### **CALCINER PROCESS VARIABLES AFFECTING CALCINED COKE QUALITY**

By the time green coke gets to the calciner most of the potential quality has already been established. Using the right calcining temperature, time and atmosphere releases the quality already built into the green coke. Again there are trade offs on calcined coke properties by adjusting these variables and blending or not blending green cokes to meet sulfur and/or vanadium specs. Just as consistent calcined coke properties allow the carbon plant to

make a more consistent anode, consistency in calciner operation variables results in a more consistent calcined coke properties. Controlling the calcination temperature is dependent on the consistency of the green coke properties (coke sizing, volatile and moisture content) as well as fuel and/or air being fed to the calciner.

The coke's porosity and bulk density is effected by the green coke's volatile content and how fast the coke is heated. This has been reported in the literature by several sources (11, 12, & 13). As discussed at the end of the section **effect of coker operations process variables on calcined coke**, even single source green cokes will vary in volatile content depending on where the coke was formed in the coke drum (14). Since larger green coke particles have lower volatile content (VM) than the smaller particles and particles segregate by particle size, how the green coke is reclaimed as calciner feed has an effect on the consistency of calcined coke. If the coke is reclaimed via a front-end loader, the coke is taken from outside the pile (larger pieces with lower VM) and then latter from inside the pile (smaller pieces with higher VM). The variation in green coke VM is even greater if different cokes are being blended to obtained a specified sulfur or vanadium content calcined coke. Blending is done to 1.) reduce the sulfur and metal content of a coke having good potential bulk density (low VM) with a coke with lower sulfur and metals but lower bulk density potential and normally higher VM and 2.) to extend the calcinable green coke supply. If there was enough green coke with desirable properties, blending would not be necessary. Because of the greater variations due to coke blends, calciners have developed techniques to blend better for a more consistent calciner feed (15). After calcining the larger calcined coke particles usually having higher sulfur and metal content will still segregate from the smaller lower sulfur containing calcined coke particles.

Using a bridge reclaimer results in a more consistent VM green coke being fed to the calciner and can increase the coke's bulk density and consistency. Since the coke's heat up rate is affected by the VM content of the green coke, the method of reclaiming the green coke will also affect the coke's bulk density. Feeding a coke with low VM followed by high VM will cause the coke to experience cycles of higher and lower heat up rate. As the green coke's VM increases, the coke will experience higher heat up rates which reduces the coke's bulk density. Using a bridge reclaimer to feed the coke to a calciner reduces the variation in green coke VM. A bridge reclaimer takes a cross section of the green coke pile and gently blends green coke from the center of the coke pile with coke from the outside edge of the coke pile. Feeding the calciner with this type of reclaiming system from coke that is dried inside a storage barn results in more consistent calcining temperature and therefore more consistent real density and bulk density calcined coke.

Real density is the preferred specification to define the degree of heat treatment coke experiences during calcination. Through the years calcined coke customers, have asked for calcined coke having different real density with a general trend of higher calcining temperatures (16). Some prebaked aluminum smelters whose system is more sensitive to anode cracking request higher real density coke, while Soderberg plants request lower real density coke. The preferred real density should be where the binder coke reactivity matches the filler coke reactivity.

Consistency of real density is desirable no matter what target average real density is chosen. Employing higher calcination temperatures will increase the coke's real density and reduce the calcined coke's reactivity. However if the temperature is too high, significant quantities of sulfur in the coke will be released increasing the coke's porosity. This will decrease the coke's bulk density and increase pitch requirement.

After calcining, the hot green coke needs to be cooled before transporting or storing in a silo. Cooling by direct water spray can add surface contaminants. Sodium and calcium are known reactivity catalysts that will increase the calcined coke reactivity (10). By reducing the levels of these elements in the cooling water or using indirect cooling, these contaminants can be controlled to very low levels. Although using butts with high sodium content will overpower the low levels of sodium from the calcined coke, some carbon anode plants are reducing the sodium content of their anodes to below 200 ppm. Since Soderberg anodes do not use butts, the reactivity of these anodes can be reduced by controlling the cooling water quality or using an indirect cooler.

**CALCINED COKE PRODUCT HANDLING (Coke sizing & impurities)**

How calcined coke is stored and transported will affect the coke sizing and can possibly add impurities. Each time the coke is moved there is additional degradation and segregation by particle size. If the handling system is not properly designed or operated at very high rates, calcined coke degradation can be significant.

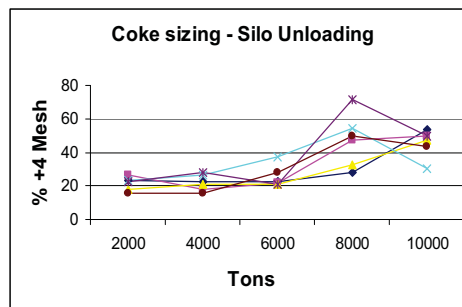
Most coke handling systems are designed efficiently (move product quickly) and often environmentally compatible (control dust emissions) but are not as sensitive to coke size degradation or segregation.

It sometimes seems that calcined coke handling systems are designed or operated to degrade the products sizing. It is logical to expect calcined coke to degrade in size if it is dropped from over 20 meters straight down into a concrete silo or cargo hold of a ship. Often the distances dropped are significantly greater than 20 meters. In addition, a device called a power trimmer is often used to make sure the outside corners of a ship's hold contains coke so no cargo space is wasted. This power trimmer increases the velocity of coke being loaded into a ship's hold. Even if great care is used in transporting the calcined coke to a ship significant calcined coke degradation can occur during ship unloading. The port where the calcined coke is unloaded is also trying to reduce their operating costs. One of those costs is ship demurrage. That is, the cost due to taking several days to empty the ship. To reduce this cost, the port may increase the rate of unloading a ship. If a vacuum unloading system is used the velocity of calcined coke is increased to unload the coke faster. This increased velocity will obviously increase calcined coke size degradation.

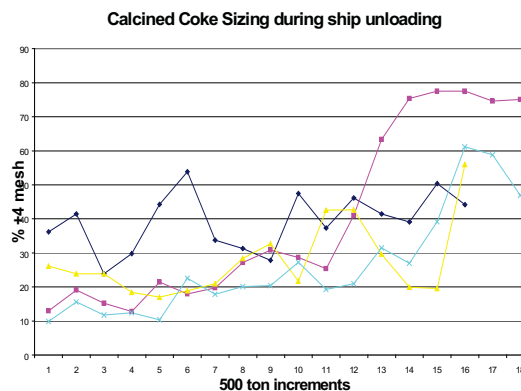
A good calcined coke degradation study was presented at the 1995 TMS meeting (17). This paper presented calcined coke sizing studies as the coke is transported or handled by different systems. All coke particles are not the same strength. The weaker particles will degrade first leaving the remaining coke less susceptible to degradation. The major degradation occurs

when coke is dropped large distances in a free fall condition. For the product studied, absolute reductions of 8% to 9% +4 mesh were observed (from 40% +4 mesh before dropping to 31% +4 mesh after being dropped 27 meters) during these free fall studies. The amount of reduction is also dependent on the strength of the coke particle, which is affected by the resid quality of the coker feed and coker conditions. This paper also conducted "soft load" tests which reduced the maximum velocity coke will reach. Using the "soft load" device resulted in less than 1% reduction in +4 mesh. The soft load device was not identified in this paper. A chokefeeder is a soft load device used to fill a ship's hold to minimize size degradation, reduce segregation during loading and eliminate the need for a power trimmer. ARCO has been using a choke feeder at it's Port of Longview calcined coke export facility since 1989. Reducing coke size degradation during ship loading is helpful but ship unloading and handling coke after unloading can more than offset the care taken to load a ship.

Particle size segregation complicates delivery of consistently sized calcined coke. Even the best designed systems incorporate multiple point feed and discharge ports resulting in significant coke segregation. ARCO studies on composite shipments have shown the first 20-40% of the coke discharged from a product silo to be approximately 15% lower in +4 mesh material than the composite sample. An example of this is illustrated in the data below.



Similar observations are found in emptying a ships hold. The first half of an unloaded hold is typically 15% less that the composite sample +4 mesh material with the second half of the unloaded hold being 15% greater. The degree of segregation can be impacted by how the silo is emptied (.ie single vs. multiple port discharge) and how the ship hold is emptied (center first increases segregation).





## REFINERY/CALCINER ECONOMICS

The petroleum refining industry has properties and pressures similar to the primary aluminium industry. Both industries require major capital investments, continue to increase production to spread the capital costs over more production and go through cycles of low product value due to periods of over capacity. The major operating cost for both industries is raw material costs.

The petroleum oil refining and marketing industry is continuously trying to improve profitability by improving refinery margins. The cost of crude oil to the refinery is approximately 80% of a refinery's operating cost. Since the revenues derived from green coke production are typically less than 2% of that number, refineries are typically driven to select a crude slate which is of the lowest quality (and hence cost) that the refinery design can accommodate.

Because of the pressure to increase refinery margins, refineries that previously made calcinable green coke and have the capability to switch to lower quality crudes will switch to fuel grade coke production. This phenomena is manifesting itself today as the price differential between lower quality crudes and higher quality crudes has widened to as much as \$5.00 to 7.00/barrel of crude. Recently, it was reported that several refiners declined to bid on the US SPC reserves that were released on this basis. (19).

Calcining operation trends indicate that margins are shrinking and that new capacity will only be cost justified economically when tied to production of steam or power. The operating and capital costs will be further increased in the future with impending environmental requirements forcing plants to reduce sulfur, nitrogen oxide, and organic compounds. In addition, local governmental agencies are requiring that coke storage be covered, placing further costs on operations.

## CONCLUSION

This paper has addressed the many factors affecting calcined coke quality. Many of the variables used in coking and calcining steps can be controlled to help provide the customer a product that can be successfully used in aluminium smelting. However, the most important variable is which crude to refine. The economic pressures of which crude to process will continue to grow and could lead to a tight calcined coke supply.

In periods of time when a refinery can only process a certain quality of crude, the refinery economics will be strongly influenced by the crude cost. This will change depending on the demand for that particular type of crude. The same can be expected for calcined coke quality. Being able to use higher sulfur and/or vanadium-nickel (crude dependent properties) containing cokes to make aluminum will provide aluminum smelters greater economic choices for calcined coke.

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