Profitable Calcining of Non-Calcinable Petroleum Coke

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Abstract

The requirement for anode grade petroleum coke is constantly growing. World wide sulfur and metal contents are increasing making it difficult for the industry to produce anodes with acceptable quality. A considerable amount of the World production of green coke, which has acceptable properties in terms of impurities, is very fine and has high amounts of Volatile Combustible Matters (VCM). Such coke can not be calcined in rotary kilns since productivity is reduced and quality of the calcined coke is unsatisfactory. Large quantities of coke with low metal and sulfur contents are burned as fuel material. China, Brazil, Argentina and Indonesia e.g. have increasing quantities of such coke available. Only China is using it for calcination by applying the Shaft Kiln Technology, a technology developed in Europe some seventy years ago which got totally forgotten in the Western calcining industry.

Hundreds of "shaft kilns" are operated in China. The technology is very simple and requires very little maintenance. The process is energy self sufficient. During calcination low loss of solid materials occurs resulting in a yield (dry basis) of 85 % (75 - 78 % for rotary kiln) and therefore CO_2 emission is 40 % lower.

Green Coke Characteristics & Capacities

Approximately 100 million tons of green coke is produced world wide (2008 figures) of which two thirds have to be considered as fuel coke which is used for power generation, the cement industry and other applications. Fuel coke typically has high sulfur (> 4%) and metal contents (V, Ni, Fe, Si, Ca) that do not allow to be used as raw material for anode production.

Twenty six million tons with higher purities (< 3% S) are used by the aluminum industry, TiO_2 production or as needle coke for steel electrodes. Besides of the impurities, the content of Volatile Combustible Matters (VCM) as well as the grain size are important factors for the calcination process. Very fine material with higher VCM's is not calcinable in rotary kilns, even if the impurity level would be acceptable. Approximately five million tons of such material is calcined in China in so called shaft kilns and another five million tons are regrettably burned. This potentially good green coke available e.g. in Brazil, Argentina, Indonesia could also be calcined, if shaft kiln technology would be introduced outside of China.

In Table 1 the properties of green coke for shaft kiln calcination versus Rotary Kiln calcination are compared.

Property	Unit	Shaft Kiln	Rotary Kiln
Water content	%	1 - 8	5 - 10
VCM	%	**10 - 16**	8 - 12
HGI		80 - 120	70 - 90
Sizing: > 16 mm	%	5 - 20	25 - 35
> 4 mm	%	30 - 55	45 - 60
< 1 mm	%	**20 - 40**	10 - 20

Table 1: Green coke properties in Shaft versus Rotary Kiln

As can be seen in shaft kilns very fine material with higher VCM's can be calcined which can not be calcined in rotary kilns where VCM's are limited to 12 %. Today's trend in the refining industry is to increase the throughput of the delayed coking unit by reducing the cycle time. The result is that green coke will be fine and high in VCM and thus only calcinable in shaft kilns.

Shaft Kiln Technology

Principle

In a "*Shaft calciner*" green coke is filled on top into individual shafts and flows by gravity through these shafts in 24 to 36 hours, resulting in a heat up rate of ~1°C per minute (compared to 50°C in a rotary kiln). Thanks to this very slow heat-up rate, green coke with high VCM (12 – 16%) contents can be calcined. The resulting calcined coke properties are excellent, with high densities, low resistivity and very coarse grain sizes.

Shaft Furnace Design

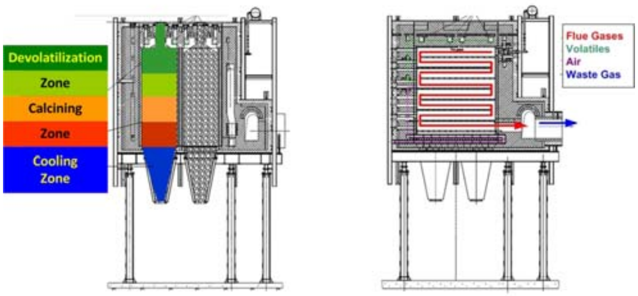

Figure 1: Shaft Furnace Concept

The main components of a shaft kiln are the vertical shafts which are heated on two sides by combustion channels equipped with baffles, similar to the flues in anode baking furnaces. In these combustion channels the volatiles are burned. An under pressure is maintained and the volatiles flow along the baffles in a downward serpentine manner. Controlled amounts of air are introduced in the flues to burn the volatiles and maintain the required temperature profile. No auxiliary fuel is required to calcine the coke.

Green coke crushed to size (< 70mm) is continuously fed on top of the shafts and is heated indirectly by the flues on both sides of the kiln. The green coke firstly passes through the preheating zone to remove moisture and some part of the volatiles. Devolatilization occurs between 500°C and 1'000 °C. Some of the volatiles are condensing inside the shafts on the cooler coke grains and glue those to larger compact lumps together. In the Calcining Zone, where the highest temperatures in the flue reaches 1'250 – 1'380°C further dehydrogenation, some desulphurization and coke shrinkage (densification) takes place. The coke moves through heated part of the the kiln in 18 – 30 hours where it finally reaches the cooling zone. With indirect water cooling a coke discharge temperature of 60 °C is reached.

Process Conditions

In Table 2 the major process parameters of a shaft kiln are compared with a rotary kiln.

Process Conditions	Unit	Shaft Kiln	Rotary Kiln
Heat-up rate	°C/min	1	50
Residence time	h	18 - 30	1
Max. coke temperature	°C	1'250	1'350
Max. off-gas velocity	m/s	1	12
Max. grain motion	m/h	0.3	1'000
Yiled:dryfeed calcined	%	85	75
CO_2 emission	tCO_2/tCPC	0.6	1.0

Table 2: Calcining Conditions Shaft Kiln versus Rotary Kiln

The shaft kiln process is characterized by its slow movement of the coke through the kiln and the slow heat-up rate. As practically no coke grains are burned or carried over into the flues the yield of the shaft kiln process is 10% higher than in rotary kilns, where considerable amounts of fine particles are entrained and burned with the off-gases in the incineration chamber. Thanks to the slow coke movement a 100 °C lower calcination temperature is possible resulting in lower desulphurization rates, less NO_x formation and a 40 % lower CO_2 emission, as no additional fuel is needed and no coke grains are burned.

Resulting Calcined Coke Quality

In Table 3 the calcined coke properties are compared between the two technologies.

Property		Unit	Shaft Kiln	Rotary Kiln
Sizing:	> 4 mm	%	**45 - 70**	**30 - 45**
	> 1 mm	%	75 - 85	60 - 75
	< 0.25 mm	%	2 - 5	5 - 10
Bulk Density	8 - 4 mm	kg/dm³	0.64 - 0.70	0.62 - 0.70
	2 - 1 mm	kg/dm³	0.76 - 0.89	0.78 - 0.86
	1 - 0.5 mm	kg/dm³	0.82 - 0.89	0.83 - 0.92
	0.5 - 0.25 mm	kg/dm³	0.85 - 0.90	0.86 - 0.93
Grain Stabiliy		%	75 - 90	70 - 85
Density in Xylene		kg/dm³	2.08 - 2.12	2.05 - 2.10
Crystallite Size		Å	28 - 35	25 - 32
Spec.electr. resistance		μΩm	380 - 500	460 - 540

Table 3: Calcined coke properties in Shaft versus Rotary Kiln

There are no big property differences to be observed except for the sizing. Real densities are similar or even slightly higher with slightly larger crystallite sizes.

It has to be remembered, that the green coke input in a shaft kiln is much finer than that for a rotary kiln. In spite of this the produced calcined coke is very coarse, as can be seen in Figure 2 below.

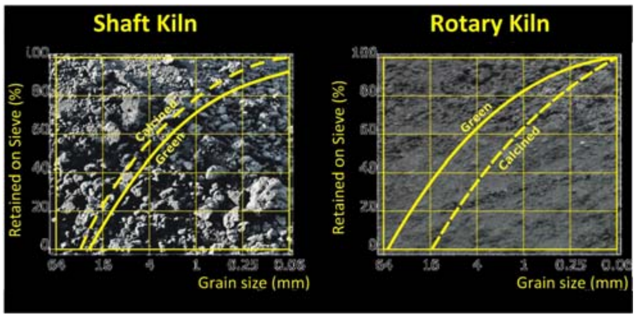

Figure 2: Grain size comparison

As explained earlier, during the calcination process volatiles condense in the cooler part of the shaft and glue the fine green coke particles together resulting in big lumps. They are calcined on their way through the kiln resulting in very coarse coke grains at the calciner outlet.

Concept of a 500’000 tpy Shaft Kiln

General Design Parameter

A shaft kiln consists of a series of shafts which are arranged in double rows. The basic design parameters are as follows:

- Annual Calcined Coke Capacity 500’000 tpy
- Required Green Coke 585’000 tpy
- Number of Kilns 16
- Number shafts/kiln 2 x 16 = 32
- Throughput per shaft 120 kg/h
- Flow time through shaft 23 – 26 h
- Max. coke temperature 1150-1250°C
- Hottest gas temperature 1’380°C
- Gas temperature at outlet 800–1000°C
- Gas volume 0.5 m^3/t
- SO_2 emission depending on S content in coke
- NO_x lower than rotary kiln as no incinerator
- CO_2 emission 40 % lower than rotary kiln
- Heat recuperation possible as steam, power generation or sea water desalination.

Plant Lay out

A 500’000 tpy plant requires a total surface of 240’000 m^2. The 16 kilns are arranged side by side with a space between the kilns. A typical lay-out as shown in Figure 3 consist of the 16 kilns, the longitudinal blending bed for green coke blending and storing and calcined coke storage silos of a size of 20’000 tons each.

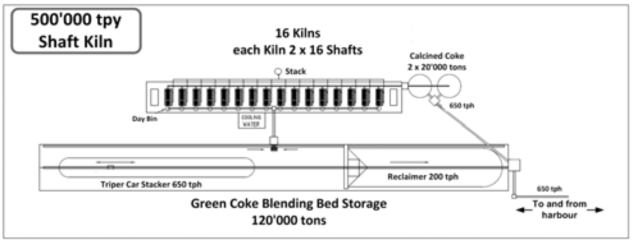

Figure 3: Typical Lay-out for a 500’000 tpy shaft kiln.

Material Handling

Green coke of the selected quality is conveyed from the harbor at a rate of 650 tph to the plant.

The **Longitudinal Blending Bed**, equipped with a travelling stacker and a bridge reclaimer is the ideal way of using a storage system for energy-efficient homogenization. In the “chevron mode”, the stockpile is formed by the stacker operating along the entire length of the bed while discharging the material. Each layer of material is discharged on top of another until full height of the stockpile has been reached. The system allows operation of the stacker and reclaimer in separate areas of the stockpile. Inclined or horizontal chain reclaimers retrieve the material from a harrow that is designed for the full height of the stockpile face. The harrow creates a cascading effect of the material down the face of the stockpile to the drag chain reclaimers, thoroughly mixing the different layers within the pile. During the time one stockpile is filled with different qualities, the other pile is reclaimed and fed directly to the shaft calciner.

The Blending Bed Technology is very well suited, when only one quality has to be produced. In case, several qualities need to be made the **“Compartmental Blending”** as often used by the industry is the better option; however it is higher in investment.

Blending Scenario

When comparing the calcined coke specifications from four Middle East Smelters they are more or less similar. The chemical specifications can only be reached, when adequate green coke blends can be made. The following blend with one Brazilian, one higher and one lower sulfur Chinese coke allows producing a calcined coke as specified by the smelters.

Green Coke	%	S %	V	Ni	Si	Fe	Na	Ca
Brasil	**50**	0.80	220	150	150	200	70	70
China 1	**25**	1.20	70	180	170	120	50	180
China 2	**25**	2.90	280	230	170	150	50	175
Average GPC		**1.45**	**200**	**180**	**165**	**170**	**65**	**125**
CPC calculated		1.35	235	210	195	200	75	150
CPC Spec (max)		3.0	250	200	200	250	100	150

Table 4: Green coke blend and resulting CPC composition

All three green cokes have VCM contents of 10 – 14 % and are very fine. As show above such cokes after calcination have excellent physical properties that meet the requirements (high bulk and real density, low electrical resistivity, coarse material etc.) of the smelters.

Calcination

At a rate of 120 kg/h green coke is fed individually to each shaft and flows slowly through it and passes through the devolatilization zone and the calcination zone where it reaches the final calcining temperature of 1'250 °C in about 18hours. At the bottom of each shaft the coke is indirectly cooled and is discharged into a vibratory conveyor from where it is transferred with the central conveyor to the calcined coke silo and later to the harbor for loading the ships for customers.

Operational Performance

A shaft kiln is an easy to operate tool. Table 5 compares some operational aspects.

Property	Shaft Kiln	Rotary Kiln
Availability	> 99 %	90 %
Downtime per year	none in 8 years	2 - 3 weeks
Refractory maintenance	practically none	considerable
Mech/electr. maintenance	very little	considerable
Fuel requirement	no fuel addition	1 GJ/t CPC
Combustion Loss	volatiles only	volatiles & coke
Manpower requirement	100/500'000 tpa	100/500'000 tpa

Table 5: Operational comparison shaft versus rotary kiln

Investment and Operating Cost Comparison

Table 6 compares major cost components between the two technologies for a 500'000 tpy calciner.

500'000 tpy Calciner	Shaft Kiln	Rotary Kiln
Investment	300 - 500 $/t	500 - 750 $/t
Production Cost		
➢ Green coke required	585'000 t	640'000 t
➢ Utilities	No add. fuel	Fuel needed
➢ Labour	same	same
➢ Maintenance mat.	Lower	Higher
➢ Miscellaneous	Same	Same
➢ Capital cost	Lower	higher
CPC production cost ~25 % lower for shaft than rotary kiln		

Table 6: Investment and operating cost comparison

Conclusion

- Shaft kiln technology allows calcination of fine and
- High VCM green coke producing a coarse CPC with a high bulk density.
- Shaft kilns have a high availability (> 99%) and a life time of 8 years with very little maintenance!
- During calcination, low losses of solid material occurs resulting in a yield of 85 %; no incinerator required (positive impact on NOx emissions!).
- The process is energy self sufficient and needs no additional energy input.
- CO_2 emission is 40 % lower than in rotary kilns (Trade possibility for CO_2 Emission Certificates)!
- Heat recuperation is possible depending on economy (steam, power or desalination).
- Comparable specific investment and production cost is 25 % lower than rotary kiln.

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