



# Petcoke Manual

**Holcim Technology Ltd.  
Cement Manufacturing**





# Petcoke Manual

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Cement Manufacturing**

**Prepared by:**

Michael Adler (CM-QPC)  
Thomas Bartlick (CM-EPT)  
Claude Diss (CM-MMT)  
Christian Engmann (CM-EPT)  
Michael Hinkel (AFR-CP)  
Rupinder Phougot (AFR-CP)  
Martin Rothfuchs (CM-EPT)  
Willi Suter (CM-QPC)  
Mirko Weber (CM-EPT)  
(PROC-CS), (HTR), (OH&S)

Holcim Technology Ltd.  
Im Schachen  
CH-5113 Holderbank  
Phone: +41 58 858 52 80

Cover photo:

Trainer Refinery, Philadelphia USA (4 delayed cokers visible in the left half of the photo)

# Preface

Thermal energy cost is one of the main cost drivers of cement production. In 2012, Holcim's expenditure on thermal energy averaged 14.65 CHF/t<sub>cli</sub>. The key factor when choosing the fuel type for a cement plant is therefore the price, and petcoke can offer a good opportunity due to its lower price compared to other traditional fuels used in the cement industry.

In addition to attractive cost savings, petcoke provides several other benefits like,

- ✓ Higher heat value in comparison to most of the traditional fuels
- ✓ Low ash content
- ✓ Consistent quality
- ✓ Being a petroleum product, it does not absorb moisture
- ✓ Ample supply, refineries are continuing to increase petcoke production to allow the refining of lower, less expensive grades of crude oil while maximizing the output of high quality fuels

On the other hand, high sulfur and low volatile matter in petcoke pose technical, operational and in some cases environmental challenges. The difficult combustion properties may increase the kiln downtime if the system is not prepared and optimized for the use of petcoke.

The purpose of this manual is to serve as a guide and reference when the user plans to either switch to petcoke or to further increase the petcoke usage. The manual contains useful information about petcoke basics, quality, operation, benchmarks, equipment design, etc. Furthermore, the user is provided with technical guidelines on how to alleviate or reduce petcoke challenges.

The manual has been developed with multi-stream contributions to ensure coverage from all relevant fields.

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## 1. OH&S

### Classification of petcoke

- Green coke (delayed coke) has a distinctive hydrocarbon smell. It can contain up to 15% volatile material, mostly hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs).
- Calcined coke purity is largely feedstock dependent. Needle coke and regular coke are calcined cokes of different purities. The needle coke being the purer form, which is used for electrodes production. Calcined coke, as a consequence of the calcining process, has a virtually zero volatile content. It is inherently a much dustier material than green coke. Depending on its use, it is usual to add a small amount (0.3 mass% or less) of high viscosity oil or a very small amount of surfactant (usually in a water solution) to act as a dust suppressant.
- Fluid coke has spherical grains and contains less volatile material than green coke. The normal grain size of fluid coke is less than 6 mm.
- Flexi coke is similar to fluid coke but contains even less volatile material and has much finer grains and thus is dustier.

### Fire explosion hazard of petcoke

- There is a slight possibility of an explosion hazard if coke in the form of dust is exposed to heat or flame.
- All forms of petroleum coke will burn if exposed to heat. The fire hazard is likely to be greater with green coke, which contains more volatile hydrocarbons than any other type of coke.
- To fight a fire of burning petroleum coke, use water, mist, foam or dry chemical.

### Suggested PPE for petcoke handling

- 3M N95 respirator
  - Exposure limit particulate PAH 0.2 mg/ m<sup>3</sup>
  - Exposure to petcoke dust 5 mg/ m<sup>3</sup> (Holcim OEL)
- Safety glasses (adequate); face shield (best)
- Protective clothing (avoid dust penetration)
  - Boots
  - Overalls
  - Gloves
- All workers exposed to petcoke should shower at the end their working shift and the use of skin cleanser and reconditioning cream is important.
- Warnings with Green coke

### If using green coke:

- Use 3M N95 activated carbon filters
- Install temperature monitors in silos
- Install inertization system for temperature control
- If stacked in the open, stack no more than 2 m high to avoid self-combustion

## 2.

### INTRODUCTION

Petroleum coke (commonly known as petcoke) is a carbonaceous solid by-product of the oil refining industry and in appearance similar to coal. Its high heat content and low ash content make it a good fuel for the cement industry. The attractiveness of petcoke to the cement industry is its lower cost when compared with other traditional fuels.

Holcim has been using petcoke since late 1980s, with several plants running on 100% petcoke substitution.

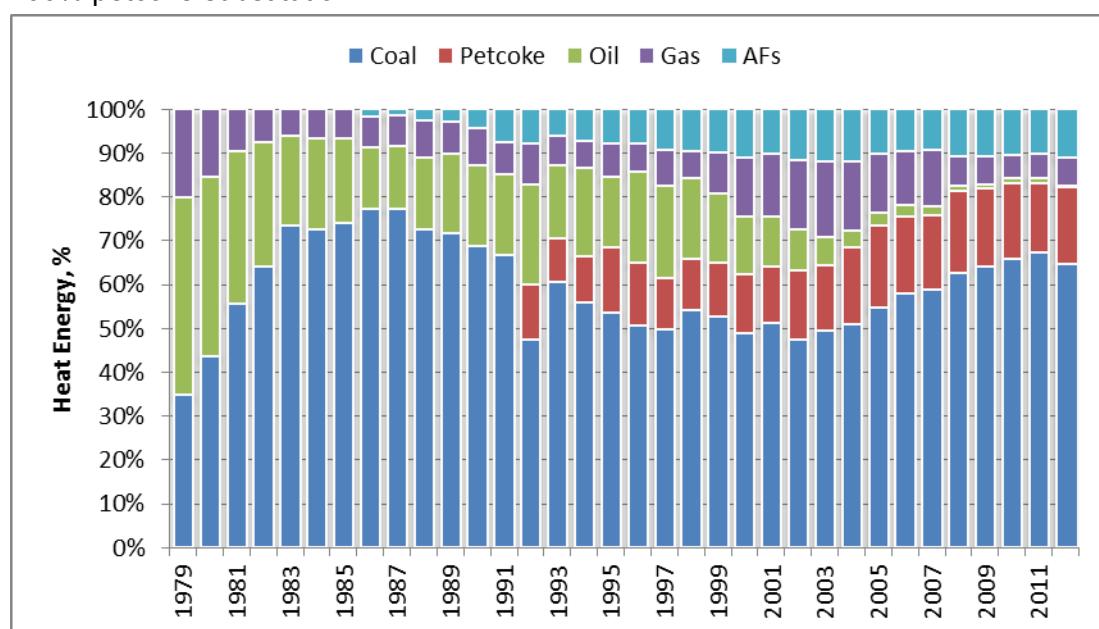


Figure 1: Kiln fuel mix for clinker production in Holcim

If the use of petcoke is to be successful, it is necessary to understand the potential for the petcoke to affect the cement production process. Different cement production processes (wet, LEPOL, pre-heater, pre-calculator) will respond in different ways and additionally this will be affected by the chemistry of the raw materials used. The properties most likely to have a direct impact on the cement production process are:

- higher sulfur content – affects operational problems due to material build-ups in the pre-heater and/or back-end of the kiln. In long or grate preheater kilns, increased SO<sub>2</sub> emissions may arise
- lower volatile matter – affects combustion and grinding efficiencies
- higher hardness – affects grinding efficiencies

This manual therefore intends to summarize:

- the situation of petcoke usage and supply in Holcim
- the physical and chemical properties of petcoke and their interactions with the cement production process
- an approach for the estimation of the petcoke potential of a specific plant
- technical guidelines and practical measures that promote and optimize the use of petcoke in the kiln process as well as in solid fuel handling and grinding
- large experience gained within Holcim group, with many kilns operating on 100% petcoke for many years

### 3.

#### **PETCOKE ORIGIN**

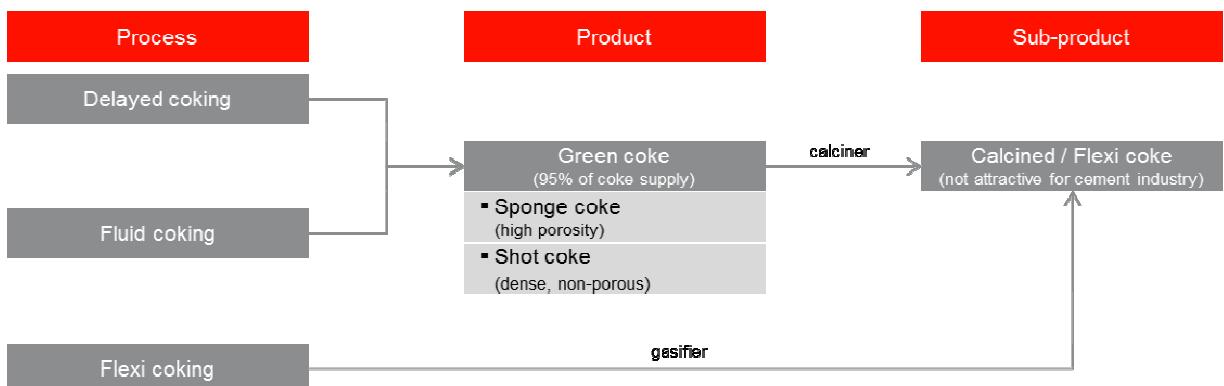
Petcoke originates from oil refining industry, wherein coking process upgrades heavy residual fraction from refining process, such as distillation or cracking, into lighter products or distillates.

Petcoke therefore contains the remaining carbon fraction of the crude oil that cannot be recovered as light product. The yield of petcoke is about 5-19 mass% depending on the crude oil stream.

There are three types of coking processes used in oil refineries:

- Delayed coker
- Fluid coker
- Flexi coker.

More than 95% of the petroleum coke is produced in delayed cokers.



### 3.1

#### **Delayed coke**

In a delayed coker, the heavy-residue feedstock is first mixed with recirculated coker vapor in the main fractionator. The fractionator bottoms stream is fed to a furnace, where it is heated up to about 480-500°C and thermally cracked. The resultant vapor/liquid mix subsequently flows into a coking drum, where the liquid fraction is precipitated and solidifies. The remaining vapors are led back to the main fractionator for separation into naphtha, light coker gas oil and heavy coker gas oil.

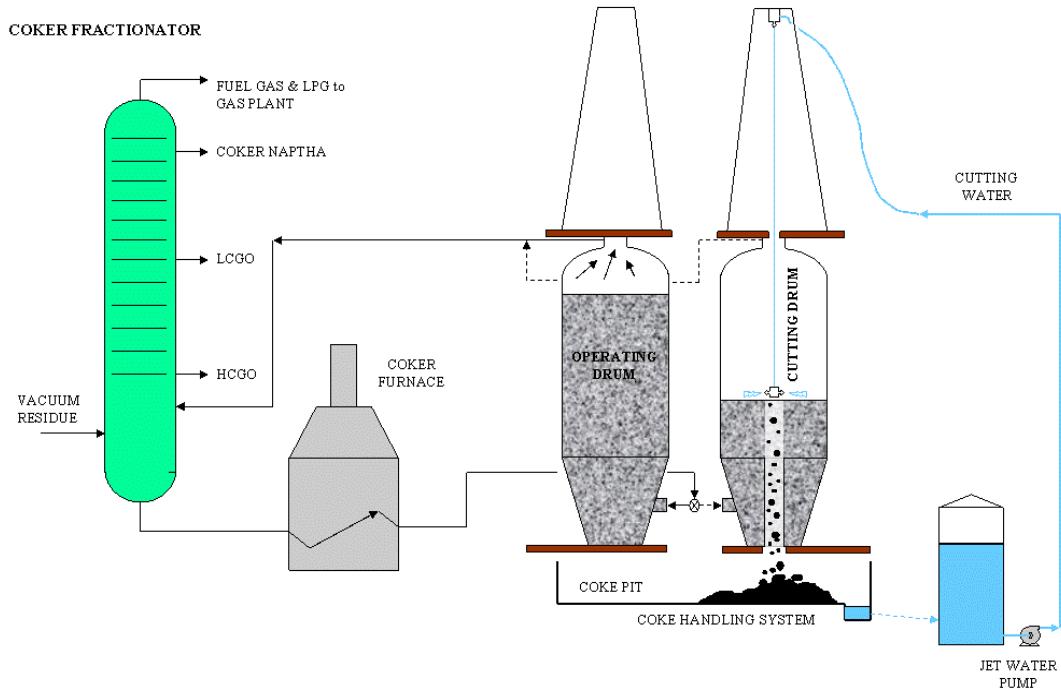


Figure 2: Typical schematic flow diagram of a delayed coking unit (source: Process Engineering Associates, Tennessee USA)

Coking chambers operate in pairs and while one coking drum is being filled, the other drum is emptied. The full drum is isolated, cooled and finally the coke is removed by drilling and cutting with high pressure water. After draining the so-called green coke is then conveyed to covered storage facilities.

### **3.2 Fluid coking**

The fluid coking process is a continuous fluidized-bed process that operates at temperatures higher than delayed coking (500-550°C). The coke formed in the reactor flows continuously to a second fluidized bed, where it is heated by partial combustion. Part of the heated coke particles is returned to the reactor to supply the energy to the endothermic crack reactions and to maintain the reactor temperature. The remainder of the coke is removed as a stream of fine petroleum coke.

### **3.3 Flexi coking**

The flexi coking process combines fluid coking with gasification to increase the yield in marketable liquid products and fuel gas. Three fluidized beds are in operation at the reactor, heater and gasifier. Coke produced in the reactor is subsequently gasified by steam and air in the gasifier. Heat for the endothermic cracking reactions in the reactor is supplied by coke combustion in the gasifier. Coke is continuously circulated between the three vessels to transfer heat. The product coke can be withdrawn from the heater bed,

## 4. GLOBAL PETCOKE MARKET

Global petcoke production is estimated to be ca. 125 Mio t/a, approximately 75% (94 Mio t) is considered to be fuel-grade. The remaining 25% is further processed for higher value end-use applications, such as anodes for aluminium industry, as a raw material for titanium dioxide production and other specialist industrial applications.

Global petcoke production is expected to grow to reach 168 Mio t/a by 2016 as refineries located in Saudi Arabia, Brazil, India, China and the USA continue to invest in new coking capacity in order to process heavier crude oils and maximize refinery yields. Compared to world coal production, estimated to be 7.8 Bio t in 2011, petcoke production is very small and only represents 1.5% of coal production.

### 4.1 Main areas of petcoke production

Worldwide approximately 40-42 million tonnes of fuel-grade petcoke is traded seaborne, with the remaining 50-52 million tonnes sold in domestic markets. The majority of global production is located at coastal oil refineries in North and South America. The Americas region is a net coal exporter and the majority of petcoke production is also exported. The main export destinations and approximate quantities are shown on the map below.

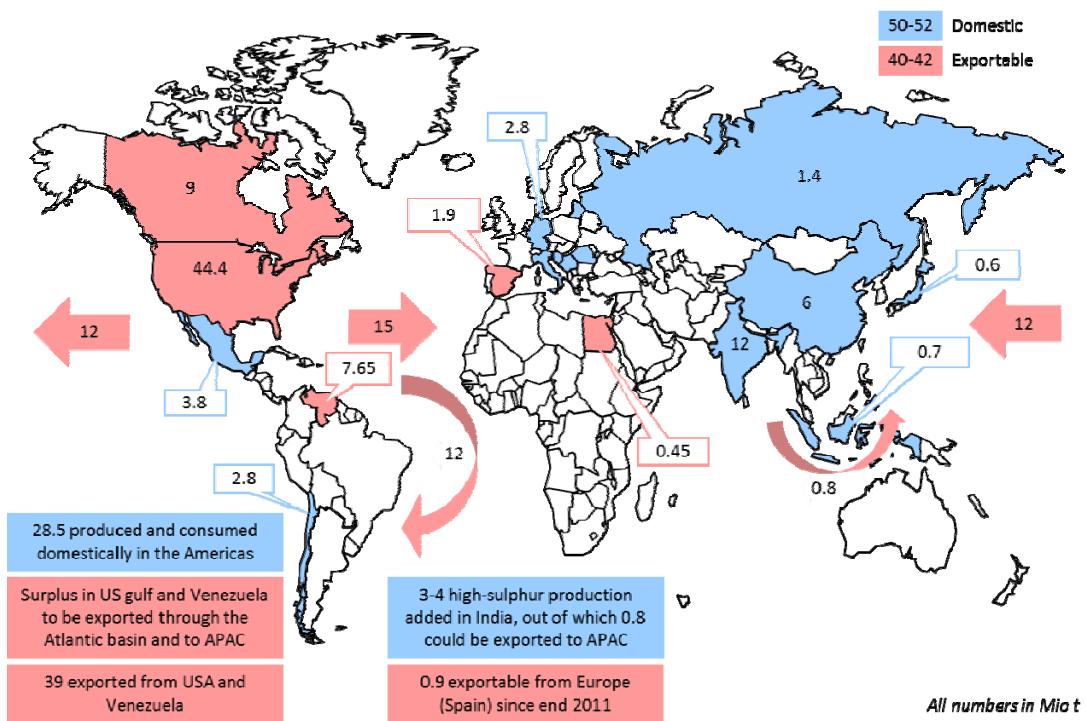


Figure 3: Total (90-94 Mio t) fuel-grade petcoke market in 2012 (source: HTR)

#### 4.2

#### Main consumers of fuel-grade petcoke

Excluding refineries' own use of petcoke either as a refinery fuel or as a fuel for co-generation, cement plants and power plants are the two main consumers of fuel-grade petcoke, with cement representing approximately half of the total demand.

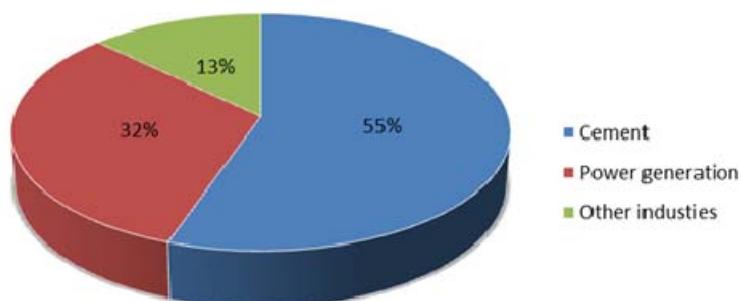


Figure 4: Fuel-grade petcoke consumption excluding own use (source: Roskill report 2010)

#### 4.3

#### Comparison of fuel-grade with coal

Fuel-grade petcoke is priced against what the market will bear. The price is capped by the equivalent energy cost (measured in Btu, kcal or GJ) of thermal coal after all other factors (i.e. switching costs) have been taken into account. At the other end of the price spectrum, petcoke is effectively a waste product from the refining process and it is therefore is "priced to move" rather than stored to sell.

In theory, oil refineries would run their cokers even if they had to pay to dispose of the petcoke due to the high market value of the light-end products (e.g. diesel, gasoline, etc.) produced from the crude oil. In addition, some refineries have strict environmental permits that limit the total quantity of petcoke they are allowed to store and this ensures that the product is priced to move it into the market.

Under balanced market conditions (fairly equal supply/demand), the price of petcoke is driven by the market price of the fuel it is substituting (i.e. steam coal). Petcoke is priced below steam coal (on a \$/GJ basis) to compensate for higher sulphur, higher HGI and the extra difficulties of the end user managing both coal and petcoke inputs. Petcoke with lower sulphur, lower metals and higher HGI (making it easier to grind) will achieve a higher market price.

Parameter	Petcoke	Coal
Market	Historically short market, tight supply / demand ratio	Possible disruptions due to 'force majeure' situations
Suppliers	Refineries and traders	Miners and traders
Price	Formula related to Pace Index (no hedge possible)	Fixed or indexed, can be financially hedged
Main users	Cement industry (> 50%), power stations, steel, aluminium, ceramics, glass	Power stations (approx. 80%), steel, aluminium, cement
Source	Venezuela, US Gulf, Spain, India, Saudi Arabia, Colombia	Colombia, USA, Russia, South Africa, Indonesia, Australia
Shipping	45% of global market is seaborne trade	700-800 Mio t out of 5 Bio t consumption

Historically, the price discount of fuel-grade petcoke compared to steam coal has varied dramatically, in the range of 8 to 68% since 2003 as shown in following graph.

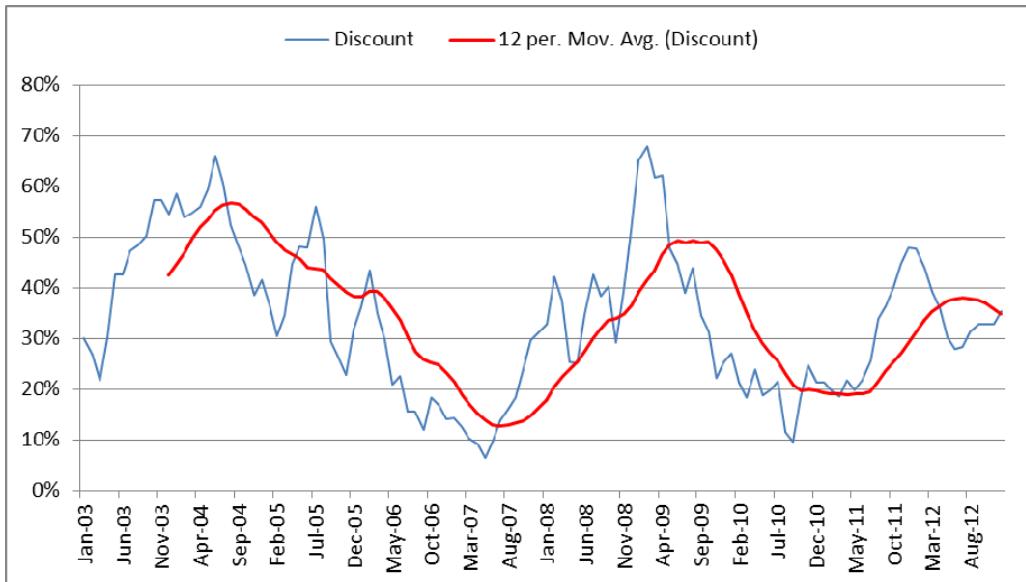


Figure 5: Petcoke discount over coal in Mediterranean market (Source: HTR)

Therefore, when considering a decision to switch to petcoke, various price scenarios should be evaluated to account for the anticipated variation in the price discount versus steam coal i.e. run a cost model based on three price scenarios (low, average and high).

Monthly updated information on petcoke prices is available on petcoke community in iShare.

#### 4.4

#### Long-term supply and demand outlook

Overall, it is expected the price differential between steam coal and petcoke is unlikely to increase substantially and very unlikely to reach the levels seen during the period 1994 to 2005, when it was in range of 30 to 70%. The prime reason for this is that the main consumers (cement & power industries) have matured in their understanding of the potential opportunities presented by petcoke substitution, to the degree that petcoke is now seen as a widely available (through international shipping) and genuine replacement for steam coal.

Many cement/power plants have made the necessary investment to handle both fuels and this interchangeability causes a much lower price differential that more accurately reflects overall cost difference between the fuels (i.e. based on factors such as energy content, sulfur levels, HGI, metals content etc.).

Price impact	Factor
↑	<b>Gasification/power projects</b> Many petcoke-fuelled gasification/power projects being developed, increasing demand for petcoke causing upward price pressure.
↓	Increasing quantities of high-sulfur petcoke will be available as existing refineries seek to take lower quality (high-sulfur) crude oils as their input material.
↓	In Asia, refineries are investing in cokers so supply capacity will increase.

#### 4.5

#### Overview of petcoke utilization in Holcim

In 2011 Holcim purchased 2.5 Mio t of petcoke, approximately 2-3% of global fuel-grade market. Approximately 1.5 Mio t was sourced through seaborne transportation, with the remaining sourced from refineries in the domestic market or neighbouring countries. The chart below shows Holcim 2011 petcoke tonnage by country and source.

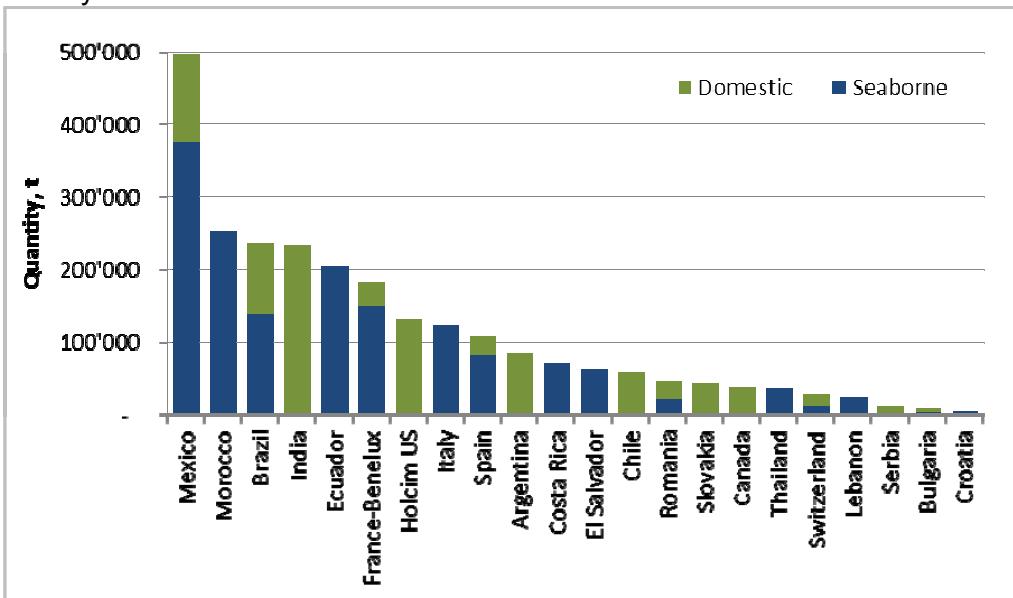


Figure 6: Petcoke quantity by source in 2011 (source: Solid Fuel Commodity Scorecard)

Holcim usage of high-sulfur petcoke is around 35% and remains much lower than our competitors (80-90%). This has the following impact:

- Holcim pays a price premium due to the restricted supply volume and high demand for low-sulfur petcoke. Furthermore, as virtually all of the announced new capacity will be high-sulfur (and low HGI) petcoke, this situation is unlikely to ease.
- Holcim is more exposed the risk of supply disruption due to the restricted supply origin of low-sulfur petcoke. The majority of low-sulfur petcoke supply is situated in Venezuela, where there is a higher risk of political instability.
- However, since 2012 Holcim has diversified some of the petcoke origins with a new contract with Repsol refinery in Spain (ca. 350'000 t), somewhat mitigating reliance on US Gulf for OpCos in Europe, Middle East and Africa.

The range and the distribution of petcoke percentage of all Holcim plants using more than 10 % petcoke of total thermal energy are shown in the following figure.

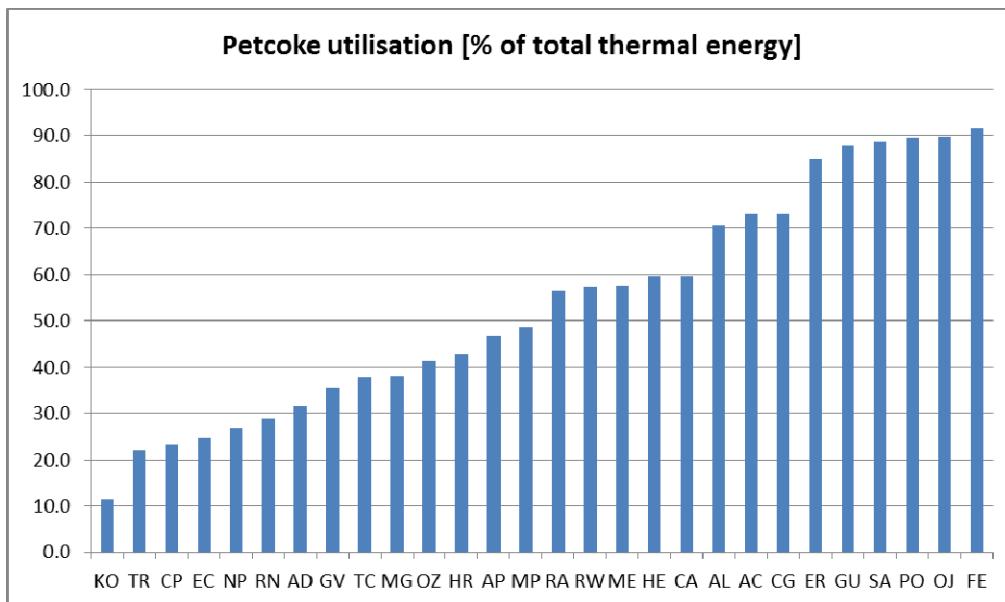


Figure 7: Petcoke utilisation of all Holcim plants using >10 % petcoke total thermal energy (ATR 2012)

The following two graphs show petcoke utilization of all and like for like<sup>1</sup> plants for the period 2008-2012.

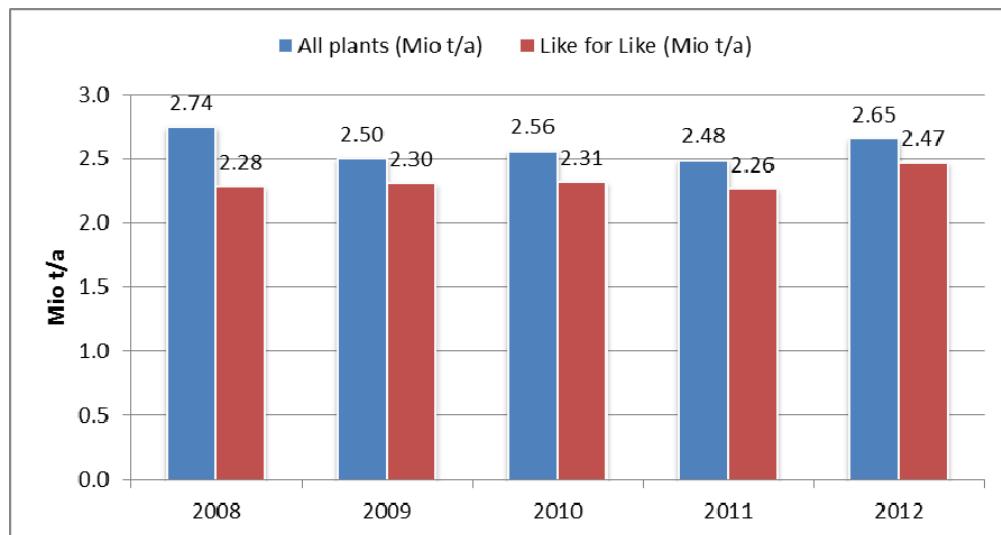


Figure 8: Overall petcoke consumption 2008-2012 (Mio t/a)

<sup>1</sup> Like for like = Plants with 5 consecutive years of petcoke utilization

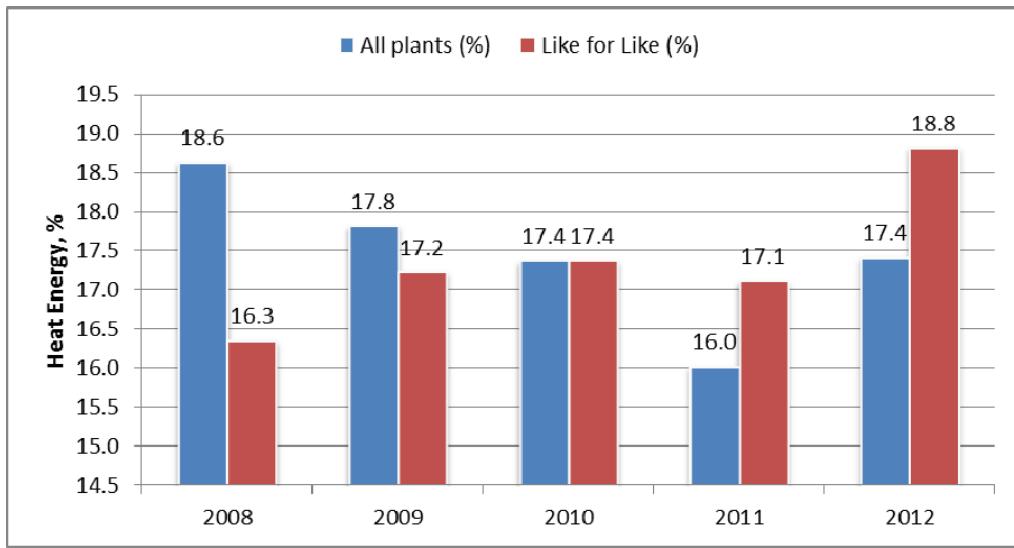


Figure 9: Overall petcoke consumption 2008-2012 (%heat energy)

The regional distribution clearly shows that LATAM has the highest petcoke consumption, covering two thirds of their total thermal energy demand by petcoke. Also many plants in Europe, North America and Africa (incl. Middle East) satisfy a significant portion of their thermal energy demand by petcoke, while in the region Asia/Oceania almost no petcoke has been consumed. The main reason being that in this region in recent years no cost effective petcoke supply has been available.

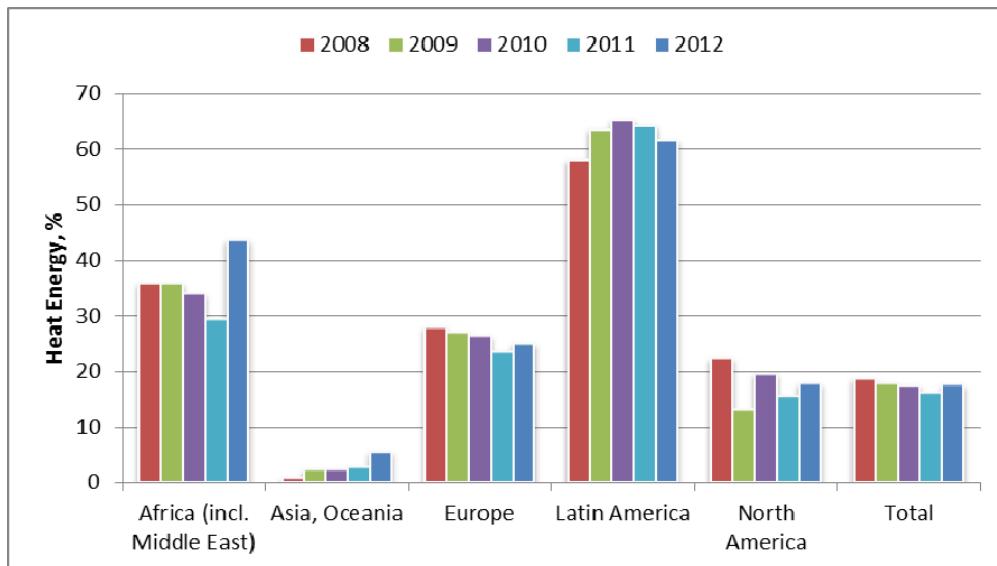


Figure 10: Regional petcoke consumption 2008-2012 for all plants (%heat energy)

About 70% of the petcoke is sourced through seaborne transportation. In 2011, petcoke was used in 24 countries with Mexico being the largest user; followed by Morocco, India, Brazil and Ecuador.

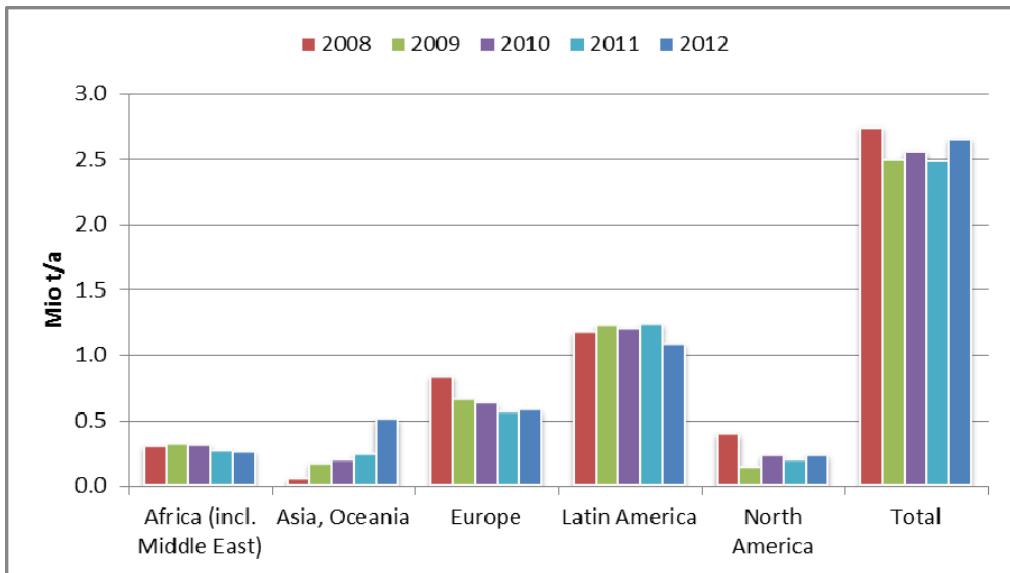


Figure 11: Regional petcoke consumption 2008-2012 for all plants (Mio t/a)

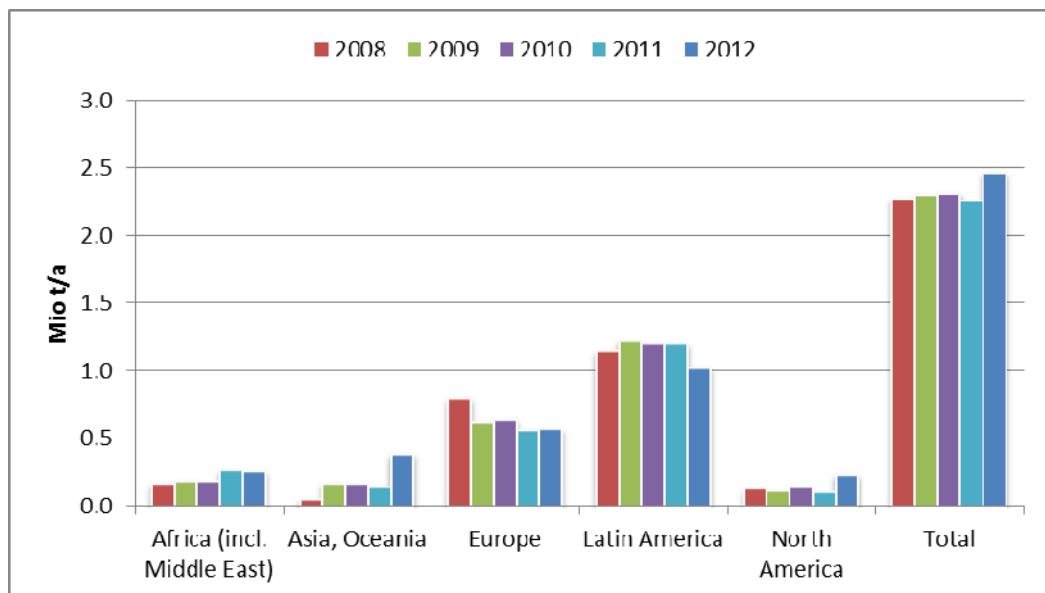


Figure 12: Regional petcoke consumption 2008-2012 for 'like for like' plants (Mio t/a)

A complete list of all the Holcim group plants consuming petcoke can be found in Annex 1.

## **5. PETCOKE PROPERTIES**

A good knowledge of the basic chemical and physical petcoke characteristics is the foundation to understand the specific requirements and impacts of petcoke on the clinker and cement production process.

Usually petcoke is a fairly homogeneous product. Nevertheless, from one source to the other its quality can vary in a certain range mainly depending on the properties of the crude oil used in the refinery, the type of coking process and the operating conditions of the coker.

The main petcoke characteristics are summarized in the subsequent chapters and compared to the corresponding properties of coal, which is typically the fuel substituted by petcoke or used in combination with petcoke.

### **5.1 Proximate Analysis**

The following parameters are measured for a proximate analysis, according to ASTM D 5142 (ISO 17246):

- Moisture (M)
- Ash (A)
- Volatile Matter (VM)
- Fixed Carbon (FC), determined by difference:  $\%FC = 100 - \%M - \%VM - \%A$

Proximate analysis	Petcoke	Anthracite	Bituminous coal	Lignite
Moisture, mass%	2-12	1-5	1-10	30-60
Ash, mass%	0.5-2	5-30	5-40	7-18
Volatile matter, mass%	1-14	3-12	15-40	15-45
Fixed carbon, mass%	80-95	60-85	35-70	10-30
Volatile matter, mass% (daf <sup>1</sup> )	1-15	<15	15-40	40-55
Fixed carbon, mass% (daf)	85-99	>85	60-85	45-60

Petcoke has typically lower moisture content when compared to most types of coal. Drying capacity of the coal mill is therefore not an issue when using petcoke.

Petcoke has a lower volatile matter content, and corresponding higher fixed carbon content when compared to most types of coal, which makes combustion (ignition and burnout) more difficult. In order to compensate for the lower volatiles, petcoke needs to be ground finer, which affects grinding capacity. On the other hand the low volatile content makes petcoke less risky to handle.

Furthermore petcoke has a significantly lower ash content compared to most types of coal. Due to low ash content of petcoke an elemental analysis of the ash is not needed for raw mix correction. Nevertheless, when switching from coal to petcoke, in most cases a correction of raw mix is required due to the lower ash content of the petcoke.

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<sup>1</sup> daf = dry and ash free

## 5.2

### Ultimate Analysis

The ultimate analysis, according to ASTM D 5373 or D 3176 (carbon, hydrogen, nitrogen) and ASTM D 4239 (sulfur) determines the actual elementary composition of the fuel (ISO 17247):

- Carbon (C)
- Hydrogen (H)
- Nitrogen (N)
- Sulfur (S)
- Oxygen (O), determined by difference:  $O = 100 - C - H - N - S - \text{ash}$

It requires special equipment, which is often not available in cement plant laboratories. Nevertheless, this kind of equipment is nowadays often part of an AFR laboratory. Even though the ultimate analysis has only limited practical value for the daily cement plant operation, it can provide an additional insight into parameters influencing burning and emission behavior of fuels.

Ultimate analysis	Petcoke	Anthracite	Bituminous coal	Lignite
Carbon, mass% (daf)	80-92	85-95	75-90	60-75
Hydrogen, mass% (daf)	0.5-3.6	1.8-4.2	4.5-6.2	4.3-6.2
Oxygen, mass% (daf)	0-0.9	2-8	3-15	20-30
Nitrogen, mass% (daf)	1.1-2.6	0.8-2.1	1.1-2.2	0.5-1.4
Sulfur, mass% (daf)	2-8	0.6-2.2	0.7-4.9	0.5-5.1

In addition to the lower content of volatiles of petcoke, the composition of the volatiles differs to those of coal. This is reflected in the lower hydrogen and oxygen content (H/C-ratio and O/C-ratio) which are a measure for the reactivity of the fuel.

The nitrogen content of petcoke is quite similar to coal. The higher NOx formation frequently observed with petcoke therefore cannot be related to nitrogen in the fuel.

The typically higher sulfur content of petcoke compared to coal can give rise to operational problems due to build-up formation in the pre-heater and/or back-end of the kiln. For certain kiln systems (long wet, long dry, LEPOL) increased SO<sub>2</sub> emissions may also arise.

The following table may be used a guideline to differentiate between different terminologies used for petcoke.

Sulfur content in petcoke	Interpretation
< 3%	Low sulfur petcoke
3-5%	Medium sulfur petcoke
> 5%	High sulfur petcoke

## 5.3

### Chlorine

Chlorine analysis is used to assess potential build-up and corrosion issues.

Generally, chlorine is very low in petcoke (<0.05%) and needs only consideration in kilns with high total chlorine inputs.

## 5.4

### Heavy Metals

Trace metal analysis is becoming increasingly more important as emission and OH&S regulations are getting stricter.

Petcoke									
Trace metals	Hg	Tl	Cd	As	Ni	Co	Se	Te	Cr
ppm	0.1-10	1-80	1	0.1-10	30-550	0.1-3	0.1-10	0.1-28	1-23
Trace metals	Cu	Mn	Pb	Sb	Sn	V	Be	Zn	Sr
ppm	1-5	1-150	1-10	0.1-10	1-30	130-2300	1-7	1-85	2-18

Petcoke can contain appreciable amounts of vanadium and nickel. For this reason the heavy metals content should be assessed prior to using petcoke from a new source. In modern preheater kilns the effect on emissions will be low due to the low volatility of these metals; however increased heavy metal contents in clinker (especially for the mentioned elements) are to be expected. Trace metal levels which would affect clinker quality have not been experienced.

## 5.5

### Calorific Value

Calorific Value (CV) of fuels, also known as the "heat of combustion" or "heat content", is the expression of the amount of energy released when the fuel is burned. It is measured in an adiabatic bomb calorimeter, according to ASTM D 5865 or ISO 1928.

The value obtained from the measurement is the gross calorific value (GCV). The net calorific value (NCV), which is relevant for the cement kiln process, must then be calculated. The difference between the Gross Calorific Value and Net Calorific Value being the condensation heat of the water evaporated during drying and formed during combustion of the fuel.

The most common method for the NCV calculation is according to ASTM D 2015:

$$NCV = GCV - 24.5 \cdot (H \cdot 9)$$

where,  
 NCV = net calorific value, kJ/kg  
 GCV = gross calorific value, kJ/kg  
 H = total hydrogen incl. hydrogen in sample moisture, mass%

Normally cement plant laboratories are not equipped to measure hydrogen or water from combustion; thus the above calculation cannot be practically applied. In place of this, an approximation method (empirically established by HTEC) can be used to determine the NCV.

$$NCV = GCV \cdot 0.981 \quad \dots \text{for petcoke} \quad NCV = GCV \cdot 0.981 \quad \text{for petcoke}$$

$$NCV = GCV \cdot 0.983 - 5.72 \cdot (15 \cdot VM) + 60 \quad \text{for coal}$$

$$NCV = GCV \cdot 0.901 \quad NCV = GCV \cdot 0.901$$

Where VM = Volatile matter, mass %

The calorific value of fuels is typically expressed in kJ/kg. Some other units are also still in use such as kcal/kg or Btu/lb. For reference,

$$1 \text{ MJ} = 10^3 \text{ kJ} = 239 \text{ kcal} = 948 \text{ Btu} \text{ and } 1 \text{ kg} = 2.204 \text{ lbs}$$

Calorific value	Petcoke	Anthracite	Bituminous coal	Lignite
GCV, MJ/kg	32-34	33-38	25-33	14-19
NCV, MJ/kg	31-33	32-36	24-32	5-15

Petcoke has a relatively high calorific value compared to most types of coal, meaning that lower fuel volumes need to be handled for the same amount of heat.

The Heat values of petcoke ranges from 28'000-35'000 MJ/t within the Holcim plants and are shown in the following figure.

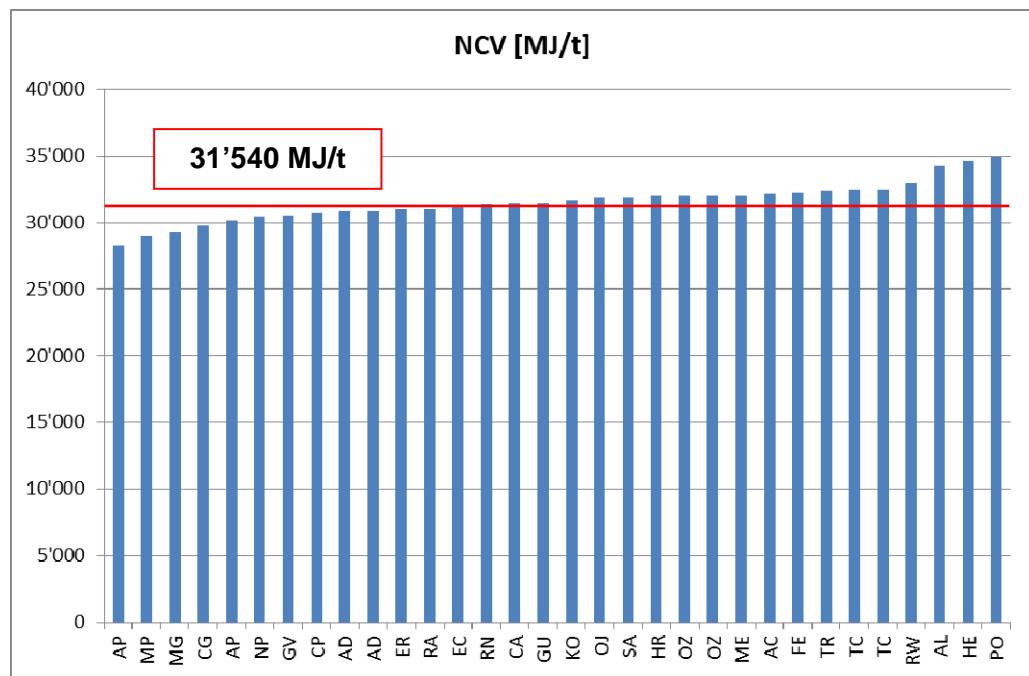


Figure 13: Net calorific value of petcoke used at Holcim plants (ATR 2012)

## 5.6

### Petcoke moisture

Petcoke typically is received at lower moisture levels than coal. Typical values of moisture content range from 2-12 %. Moistures of all Holcim plants are shown in figure below.

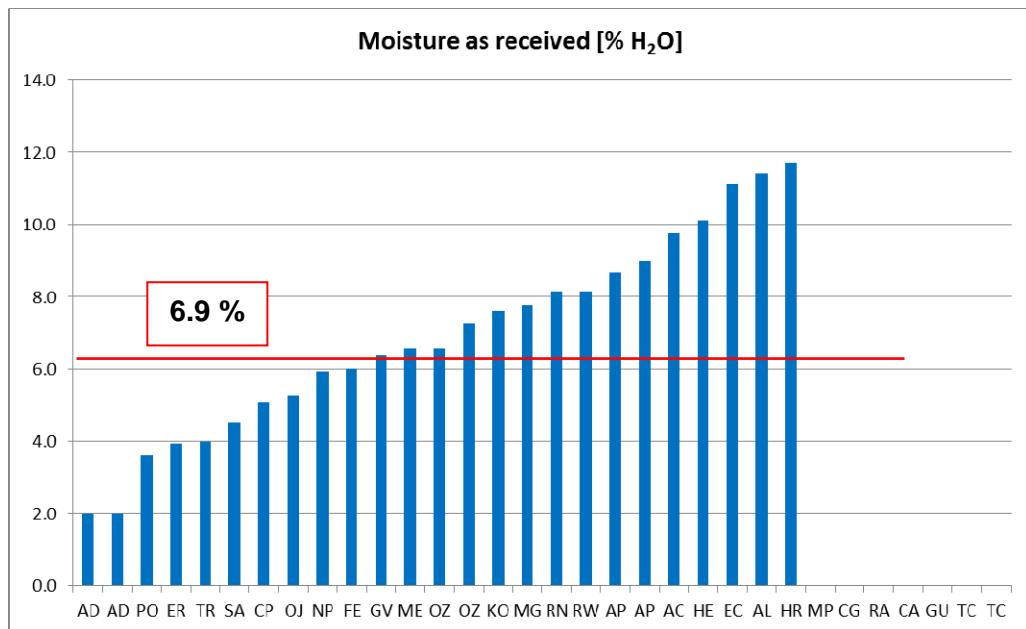


Figure 14: Petcoke feed moisture at Holcim plants (ATR 2012)

## 5.7

### Petcoke volatiles

Petcoke typically contain low volatiles in the range of 10 %. Figure below shows typical volatile content in petcoke at various Holcim plants.

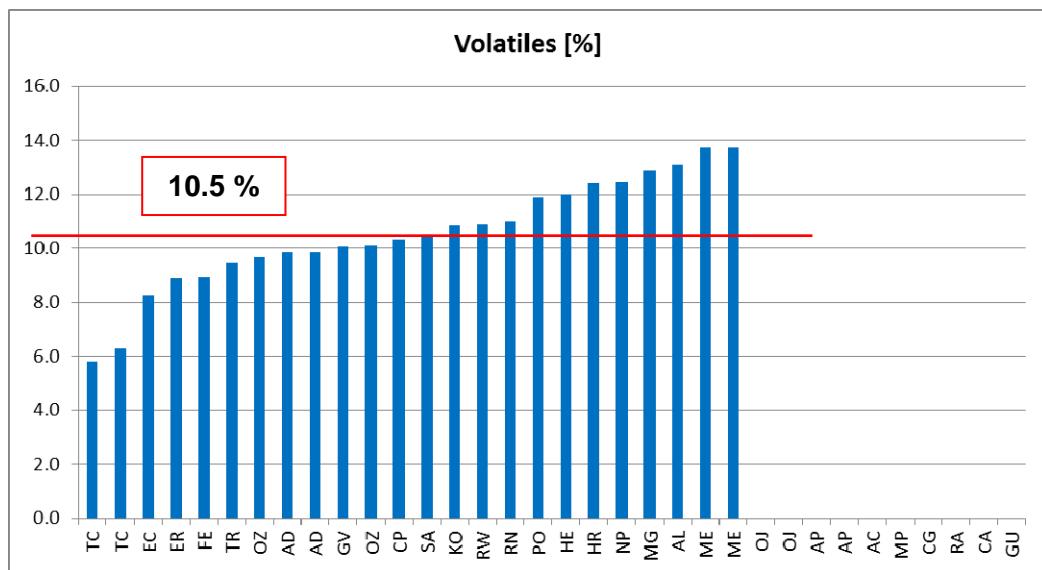


Figure 15: Volatiles in petcoke at Holcim plants (ATR 2012)

## 5.8 Bulk density

Normal-quality green coke is characterized by a high porosity and anisotropy<sup>1</sup>. Due to its high porosity, this type of petcoke is also called sponge coke. However, a dense non-porous isotropic<sup>2</sup> petcoke results if the feedstock of the coking process is rich in high molecular asphalt. This type of petcoke is also called shot-coke.

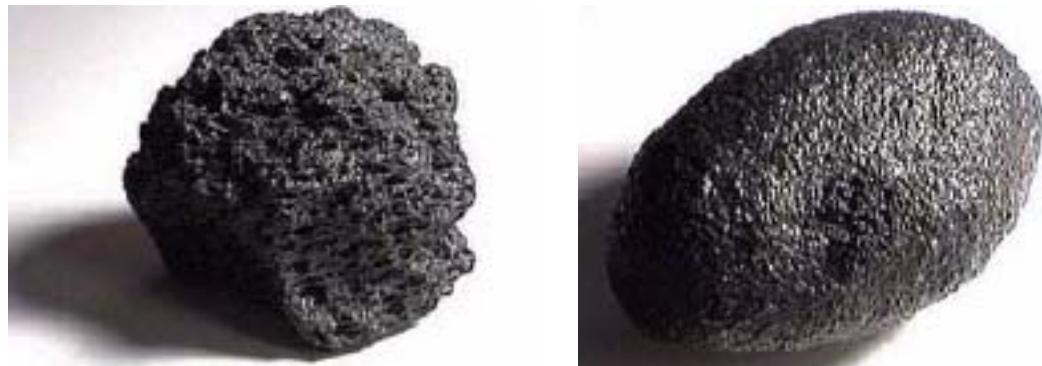


Figure 16: Sponge coke (left) and shot coke (right)

	Sponge coke	Shot coke	Anthracite	Bituminous coal	Clinker
Bulk density, t/m <sup>3</sup>	0.8-0.9	1.2-1.4 ?	0.8	0.7	1.2

## 6. QUALITY CONTROL

The purpose of controlling solid fuel quality has four aspects:

- 1) Incoming control to ensure suppliers meet their specifications
- 2) Kiln operation: heat supply, flame properties, build-up and ring formation
- 3) Clinker quality optimization: ash and SO<sub>3</sub> incorporation
- 4) Mill control

### 6.1 Incoming control

Sampling and analysis of solid fuels arriving at the plant should be made periodically to ensure supplier compliance with regards to the agreed solid fuel quality. The frequency of sampling and analysis, along with the required analyses will differ depending on the situation (supplier agreement, critical elements for the kiln, consistency of supply etc.).

Recommended is a manual composite sample per delivery for measurement of moisture, CV, volatile content, ash content and sulfur (plus chlorine in critical kilns). Representative sampling of arriving shipment should be ensured, and ASTM D 346 provides guidance for collecting and preparing samples for laboratory analysis.

<sup>1</sup> Anisotropic = having unequal physical properties along different axes

<sup>2</sup> Isotropic = having uniform physical properties in all directions

## 6.2

### **Process Control**

For mill and kiln process control purposes regular solid fuel samples leaving the coal mill should be taken. The frequency of sampling is normally between 4-8 hours depending on the observed variability.

Samples are typically taken by automatic or manually operated screw samplers installed along the transit from the mill to the fine coal silo. The sampling device should include a safety air lock and conform to appropriate ATEX requirements. Manual sampling (i.e. without a screw sampler) of fine petcoke is not recommended. Depending on the degree of automation, the sample can be transported to the laboratory either manually or via pneumatic tube system. If opting for a tube system, a separate coal/petcoke receiving station in the lab is recommended due to the fine dusts associated with it.

On each sample, fineness ( $R_{90\mu\text{m}}$  and  $R_{200\mu\text{m}}$ ) and moisture content are normally sufficient for appropriate mill and kiln process control. Then from each sample a daily composite sample should be made for more detailed analysis including:

- Calorific value
- Volatile matter
- Ash content (and composition if >5%)
- Sulfur content
- Total carbon content
- Chlorine (in critical kilns)

## 7.

### **PETCOKE POTENTIAL**

A good understanding of the different factors limiting the use of petcoke is essential to determine the potential of a specific plant for petcoke utilization. The main properties of petcoke with a direct impact on the clinker production process are:

- **high sulfur content** – affects clinker quality, kiln operation (build-up and ring formation) and emissions (increase in SO<sub>2</sub>)
- **low volatile matter content** – negatively affects combustion and requests finer grinding
- **high hardness** –reduce grinding capacity

Therefore, the maximum petcoke potential of a certain plant, i.e. kiln and mill system, is determined by:

1. **Sulfur limit** – maximum sulfur input that can be managed by the kiln system
  - a. Chemical limit: maximum sulfur incorporation into clinker
  - b. Kiln operational limit: maximum sulfur content in hot meal
  - c. Emission limit: SO<sub>2</sub> emission permit limit
2. **Combustion limit** – maximum rate that can be burned completely
3. **Grinding limit** – maximum rate that can be ground to the required fineness

In a first approach the sulfur limit will be considered, assuming that the combustion and grinding limits can be overcome by optimization and modification of the kiln and mill system. This will be further elaborated in sections Petcoke Grinding and Petcoke Combustion.

## 7.1

### **Chemical limit (sulfur incorporation into clinker)**

The chemical limit for sulfur input to the kiln system is given by the maximum chemical potential of the clinker to bind sulfur. The host phases for sulfur in clinker are:

- **Alkali-sulfates** (K<sub>2</sub>SO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub>) – The sulfur reacts preferably with any alkalis, potassium and sodium, to produce alkali sulfates.
- **Anhydrite** (CaSO<sub>4</sub>) – If there is an excess of sulfur over alkalis the remaining sulfur reacts with calcium to produce anhydrite.
- **Ca-Langbeinite** (K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) – Anhydrite can react further with potassium sulfate to form the double salt Ca-Langbeinite providing an additional mineral phase to incorporate sulfur into clinker with less alkali than the alkali sulfates.
- **Belite** (C<sub>2</sub>S) – Minor amounts of sulfur (<0.8% in belite) can also be incorporated into belite. It is believed that incorporation of sulfur into belite can partially stabilize belite causing reduced alite formation.

As the main host phases of sulfur are combinations with alkalis, the chemical limit for sulfur incorporation in clinker is to a large extent determined by the amount of alkalis available.

The total sulfur input, from raw materials and fuels, therefore needs to be viewed in relation to the total alkali input. The molar balance between alkalis and sulfur in clinker is expressed by the Alk/SO<sub>3</sub> ratio:

$$\frac{Alk}{SO_3} = \frac{\frac{K_2O}{94} + \frac{Na_2O}{62} - \frac{Cl}{71}}{\frac{SO_3}{80}}$$

where,  
 K<sub>2</sub>O = K<sub>2</sub>O in clinker, mass%  
 Na<sub>2</sub>O = Na<sub>2</sub>O in clinker, mass%  
 Cl = Cl in clinker, mass%  
 SO<sub>3</sub> = SO<sub>3</sub> in clinker, mass%

If only the formation of alkali sulfates (K<sub>2</sub>SO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub>) and a minor incorporation of sulfur into belite are taken into consideration, a minimum Alk/SO<sub>3</sub> ratio of 0.8 would be achievable. But the formation of Ca-Langbeinite allows reaching also Alk/SO<sub>3</sub> ratios significantly below 1, as one unit of potassium is able to combine with the equivalent of 3 units of sulfur.

In addition the chlorine level in the clinker needs to be taken into consideration. Alkalies have a higher affinity with chlorine compared to sulfur and therefore the alkalies in the form of alkali chlorides are not available anymore to combine with sulfur.

Thus the chemical limit for the sulfur incorporation into clinker can be calculated as theoretical maximum SO<sub>3</sub> in clinker or minimum Alk/SO<sub>3</sub> ratio:

$$(SO_3)_{max} = 3 \cdot 0.85 \cdot K_2O + 1.29 \cdot Na_2O - 1.13 \cdot Cl \quad ^1$$

$$\left(\frac{Alk}{SO_3}\right)_{min} = \frac{\frac{K_2O}{94} + \frac{Na_2O}{62} - \frac{Cl}{71}}{3 \cdot \frac{K_2O}{94} + \frac{Na_2O}{62} - \frac{Cl}{71}}$$

### Example

Clinker: 1.05% SO<sub>3</sub>, 0.94% K<sub>2</sub>O, 0.26% Na<sub>2</sub>O, Alk/SO<sub>3</sub> = 1.08

Chemical maximum SO<sub>3</sub> in clinker, SO<sub>3,max</sub> = 2.73

Chemical minimum Alk/SO<sub>3</sub> ratio in clinker, (Alk/SO<sub>3</sub>)<sub>min</sub> = 0.42

Figure 17 shows NaO<sub>2</sub> eq vs. SO<sub>3</sub> graph of Holcim group (main clinker produced at each plant, ATR 2011) with RED line indicating Alk/SO<sub>3</sub> ratio of 1.0. It can be seen that a large number of Holcim plants have an excess of alkalies over sulfur indicating additional potential for petcoke use.

<sup>1</sup> 0.85, 1.29 and 1.13 are molecular weight ratios of SO<sub>3</sub>/K<sub>2</sub>O, SO<sub>3</sub>/Na<sub>2</sub>O and SO<sub>3</sub>/Cl respectively.

In case of an excess of alkali over sulfur the alkalis will be integrated into  $C_3A$ . This leads to the formation of orthorhombic instead of cubic  $C_3A$ , which may cause abnormal setting behavior of cement. Therefore a significant excess of alkali over sulfur needs to be avoided.

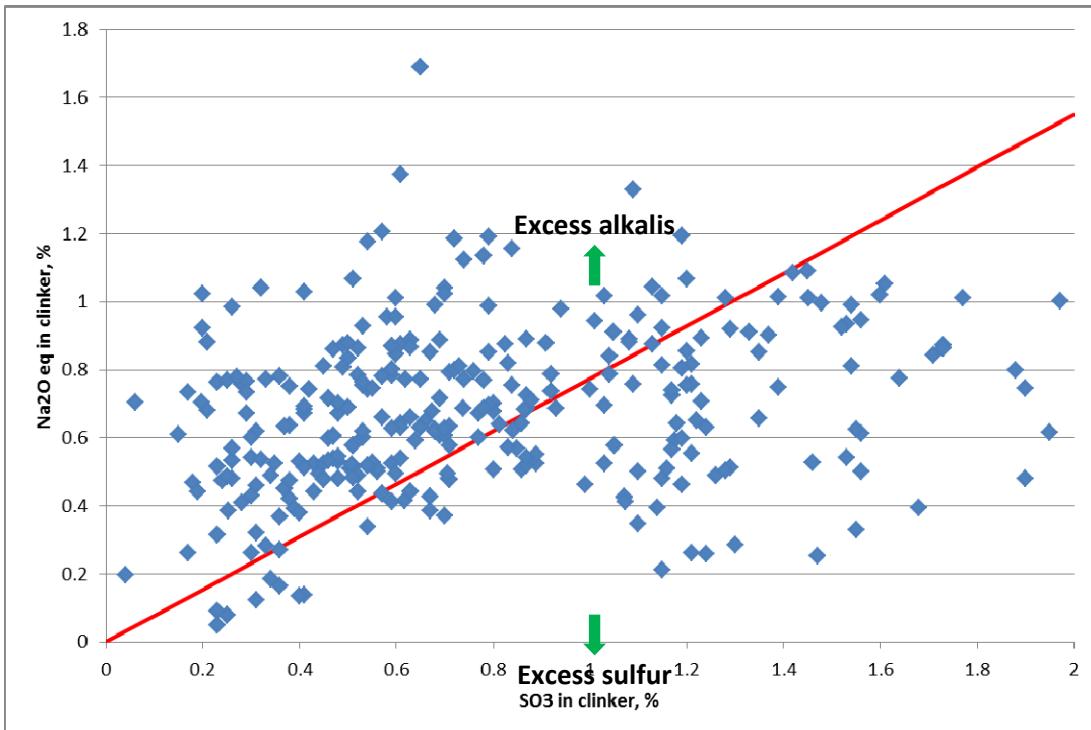


Figure 17: Clinker  $SO_3$  vs.  $Na_2O_{eq}$  of Holcim plants in 2011

## 7.2

### Operational limit (sulfur volatilization)

The operational limit for the sulfur input is determined by the ability to control sulfur volatilization to prevent ring and build-up formation in the kiln system.

The different host phases of sulfur have different thermal stabilities before they are broken down again and volatilize:

- **Alkali-sulfates** ( $K_2SO_4/Na_2SO_4$ ) – relatively stable at temperatures up to  $1650^\circ C$ .
- **Anhydrite** ( $CaSO_4$ ) – occurs only rarely in clinker as it is very temperature sensitive and breaks down to large extent already at typical burning zone temperatures of  $1450^\circ C$ .
- **Ca-Langbeinite** ( $K_2Ca_2(SO_4)_3$ ) – relatively stable at temperatures up to  $1520^\circ C$ .

The required material temperature in the burning zone of the kiln depends strongly on the raw meal burnability. A good burnability of the raw meal allows the clinkering reactions to take place at lower temperature, and therefore also stabilizes the alkali sulfates.

Besides temperature sulfur volatilization is strongly influenced by the burning regime in the kiln, namely the kiln atmosphere. A sufficiently high oxygen level in the kiln

atmosphere and avoidance of local reducing conditions favors the stability of the alkali sulfates.

As a third important factor influencing sulfur volatility we need to mention also "time" of exposure to temperatures above thermodynamic stability limit.

To monitor the sulfur volatility, measurements on hot meal should be made. The frequency of sampling is determined by process requirements, but normally every 4 hours, or every 8 hours for problem-free kilns. Parameters measured on hot meal are:

- Loss on ignition
- SO<sub>3</sub>
- Chlorine
- K<sub>2</sub>O
- Na<sub>2</sub>O

The hot meal sample should ideally be taken approx. 30 minutes (residence time of clinker in cooler) before the clinker sample, so that both samples reflect the same process conditions.

The sulfur volatility can then be calculated by:

Sulfur volatility,		Interpretation
$\varphi$		
	<0.5	Ideal for high petcoke use
	0.5-0.7	OK
	0.7-0.9	Combustion problems
	>0.9	Serious combustion problems

where,  $\varphi$  = Sulfur volatility, -  
 $SO_3_{cli}$  = SO<sub>3</sub> in clinker, mass%  
 $LOI_{cli}$  = Loss on ignition of clinker, mass%  
 $SO_3_{HM}$  = SO<sub>3</sub> in hot meal, mass%  
 $LOI_{HM}$  = Loss on ignition of hot meal, mass%

The following graph can serve as a guideline for dry process kilns on how critical the build-up situation can get depending on the level of sulfur and chlorine in hot meal.

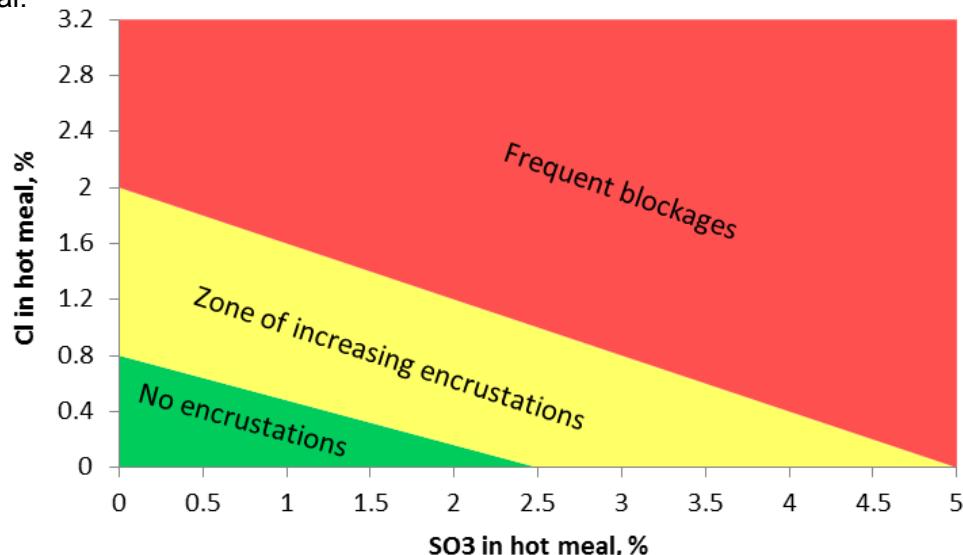


Figure 18: Guide values for max. tolerable hot meal concentrations (applicable to SP/PC<sup>1</sup> kilns only)

As a rule of thumb, the SO<sub>3</sub> concentration in the hot meal should be kept below 3.5% (max. 5%, assuming Cl < 0.5%), otherwise build-ups will become problematic even with intense cleaning. Considering this maximum acceptable sulfur levels in hot meal and typical levels of sulfur volatilization (0.5-0.7), the maximum sulfur input can be calculated.

$$SO_{3,cli,max} = (1 - \varphi_{min}) \cdot SO_{3,HM,max} \cdot \frac{100 - LOI_{cli}}{100 - LOI_{HM}}$$

### Example

SO<sub>3</sub> HM, max = 4 %, LOI<sub>cli</sub> = 0%, LOI<sub>HM</sub> = 14%

Minimum achievable sulfur volatility  $\varphi$ : 0.6

Operational maximum SO<sub>3</sub> in clinker: SO<sub>3</sub> cli, max = 1.86%

## 7.3

### Emissions limit

Depending on the type of kiln system, the SO<sub>2</sub> emissions might limit the maximum sulfur input to the kiln system. Additionally, NO<sub>x</sub> increase due to substitution by petcoke can also limit the petcoke potential.

In dry process kilns with suspension preheater, the sulfur scrubbing effect of the preheated material in the cyclones is very efficient. Furthermore there is additional sulfur absorption in the conditioning tower and in the raw mill during compound operation. This means that in general no sulfur from fuel is contributing to the emissions in preheater and pre-calciner kilns.

An exception is preheater and pre-calciner kiln systems equipped with a gas bypass. In this case, the kiln gases highly enriched in SO<sub>2</sub> have the opportunity to

<sup>1</sup> SP = Suspension preheater, PC = Precalculator

bypass the suspension preheater, conditioning tower and raw mill, all of which have the “scrubbing effect”.

In grate preheater kilns (LEPOL), a relatively good scrubbing efficiency can still be achieved. However, the sulfur absorption is far less effective in long dry kilns. Almost no absorption is observed in wet kilns and an increase in SO<sub>2</sub> emissions is therefore expected. The influence of petcoke on emissions is discussed in more detail in the section 10.8.

#### **7.4 Guide values for maximum sulfur input**

Based on the above considerations on the factors limiting the sulfur input to the kiln system as well as best practices within the Holcim plants the following kiln type specific guide values for a minimum Alk/SO<sub>3</sub> ratio and maximum sulfur level in clinker have been defined:

Kiln system	Max. sulfur in clinker %SO <sub>3</sub> cli	Min. Alk/SO <sub>3</sub> ratio
PC – Pre-calciner	2.0	0.4
SP – Suspension preheater	1.7	0.5
DG – Grate preheater (Lepol)	1.2*	**
DL – Long, dry	1.1*	**
WL – Long, wet	1.0*	**

For kiln systems without bypass or kiln dust removal and with low levels of pyrite in the raw material, the maximum sulfur level in clinker is equal to the maximum total sulfur input (raw material and fuels). Otherwise the maximum total sulfur input to the kiln system can then be calculated as:

$$\text{Max. Sulfur Input} = \text{SO}_{3\text{cli,max}} + \frac{m_{CKD}}{m_{cli}} \cdot \text{SO}_{3\text{CKD}} + \frac{m_{KF}}{m_{cli}} \cdot \text{SO}_{3\text{pyrite}}$$

where,       $\text{SO}_{3\text{cli,max}}$  = Max. SO<sub>3</sub> in clinker, mass%

$m_{CKD}$  = mass flow of cement kiln dust (CKD), t/h<sup>1</sup>

$m_{cli}$  = mass flow of clinker, t/h

$\text{SO}_{3\text{CKD}}$  = SO<sub>3</sub> in CKD, mass%

$m_{KF}$  = Mass flow of kiln feed, t/h

$\text{SO}_{3\text{pyrite}}$  = Pyritic SO<sub>3</sub> in kiln feed, mass%<sup>2</sup>

For a detailed assessment of a plant situation, an Alk/SO<sub>3</sub>/Cl balance, evaluation of sulfur volatility and sulfur emissions should be carried out.

In suspension preheater and pre-calciner kilns, the maximum sulfur input is mainly limited by the operational or chemical limit. A significant excess of sulfur over alkalis can be achieved if the design and operating conditions of the kiln allows a good control of the sulfur volatility.

Pre-calciner kilns have even a higher potential for sulfur intake, as the sulfur volatility can be better controlled due to the lower material residence time in the

<sup>1</sup> Not recirculated back to the kiln system e.g. filter dust extraction or bypass dust

\* Not a limiting factor, as usually the emission limit kicks in before max. sulfur in clinker becomes critical.

\*\* Not a limiting factor, as usually the emission limit kicks in before Alk/SO<sub>3</sub> ratio becomes critical.

<sup>2</sup> Assuming no pyritic sulphur going into emissions

rotary kiln and the possibility to maintain higher kiln inlet O<sub>2</sub> levels in kilns with in-line calciners (ILC). Special attention is required for preheater and pre-calciner kilns with a gas bypass where sulfur rich gases can escape through the bypass and lead to an increase of SO<sub>2</sub> emissions.

In grate preheater kilns, long dry kilns and wet kilns the potential for sulfur input is rather limited by the emission limit. The scrubbing of the exhaust gases in a grate preheater or chain system is by far not as efficient as in a suspension preheater. The removal of filter dust (CKD) in long and intermediate dust in grate preheater kilns can be an effective measure to withdraw some sulfur from the kiln. Nevertheless a sustainable method for re-utilization of the dust, preferably as filler in the cement, needs to be ensured.

## 8.

### **PETCOKE GRINDING**

Petcoke is widely used within Holcim if available. It is characterized by high calorific value, moderate moisture, high sulphur, low ash and low volatiles.

Its hardness and potential unfavourable properties for grinding may create capacity problems in existing grinding installations or new projects. Hence coals mills must be assessed before switching from coal to petcoke grinding.

In most cases the petcoke is co-ground with coal and the ground petcoke-coal mixture is used for calciner or calciner and main burner. Using a mixture may be a consequence of:

- Insufficient capability of increasing sulphur input via petcoke
- Lack of availability of petcoke
- Lack of coal/petcoke grinding capacity.

The following chapter deals with all issues related the grinding process and its necessary auxiliary processes where petcoke may differ from coal grinding.

## 8.1

### **Petcoke Storage, Preparation and Handling**

#### 8.1.1

##### **Storage issues**

Petcoke is usually stored in separate stockpiles or separate sections of one long stockpile in case of using a tripper belt and a side reclaimer.

Basically raw and fine petcoke with a range of only 8 – 14% VM doesn't cause trouble during handling and storage as tendency of auto combustion is low.

An exception was a reported smouldering fire in raw petcoke storage. (Chekka, September 2012). Raw petcoke from two vessels started to burn in the yard and the fire had to be extinguished with dust. Most probably the purchased petcoke was not the normal "green" or uncalcined but partly calcined petcoke. Releasing volatiles during the calcination process in the oil refinery creates micropores in the petcoke being responsible for water absorption properties of coke and petcoke. The absorption process is exothermic and could cause auto-combustion especially in hot environment. (A. Schönbucher, 2002: Thermische Verfahrenstechnik: Grundlagen und Berechnungsmethoden für Ausrüstungen und Prozesse [Thermal Process Technology / Basics and Calculation Models for Equipment and Processes])

The „IMSBC-Code“ (International Code for shipping bulk material offshore from 2009 with latest updates from 2012) is dealing with potential hazards of bulk material. This document states that petcoke is a hazardous material in case of having a temperature beyond 55°C. In that case following measures have to be taken for loading petcoke into a vessel:

- In case of > 1 m layer in the vessel the first layer of 0.6 to 1.0 m must have < 55°C. The rest can have a higher temperature.
- Petcoke > 107°C must not be accepted for loading in a vessel.

In case of having autogenous combustion with coarse petcoke it is important to contact the shipping company for the material temperature when loading the vessel. The plant should refuse petcoke  $> 107^{\circ}\text{C}$  material temperature during loading the vessel,

Another case was observed in 2013 (Guayaquil). The plant reported smoldering fires in the covered petcoke storage. During an inspection of the storage in December 2013 a section of about 5 m x 1 m of coarse petcoke was glowing as shown in the following figure.



Figure 19: Glowing petcoke at the toe of the covered petcoke storage of Guayaquil plant. The red area is burning; the brown layer is ash covering the burning coal. (December 2013)

The source of the petcoke was the refinery in Venezuela. Probably partly calcined petcoke with its exothermic water absorption was responsible for this behaviour.

Like for smoldering coal the glowing petcoke has to be extracted with an excavator or front end loader, disposed and covered with inert material until the fire is extinguished. This kind of fire cannot be extinguished with water due to the risk of a water gas explosion.

#### 8.1.2 Mixing of raw petcoke and coal

In case a mixture of coal and petcoke is used, preparation is required to achieve uniformity in ash and net calorific value.

#### 8.1.2.1 Solution with one raw fuel silo and one transport to the silo only

Separately stockpiled coal and petcoke are volumetrically proportioned and mixed with a front-end loader (FEL) before feeding to a raw fuel silo of the mill. After grinding, the mixture of ground coal and petcoke is stored in respective bins for kiln and calciner.

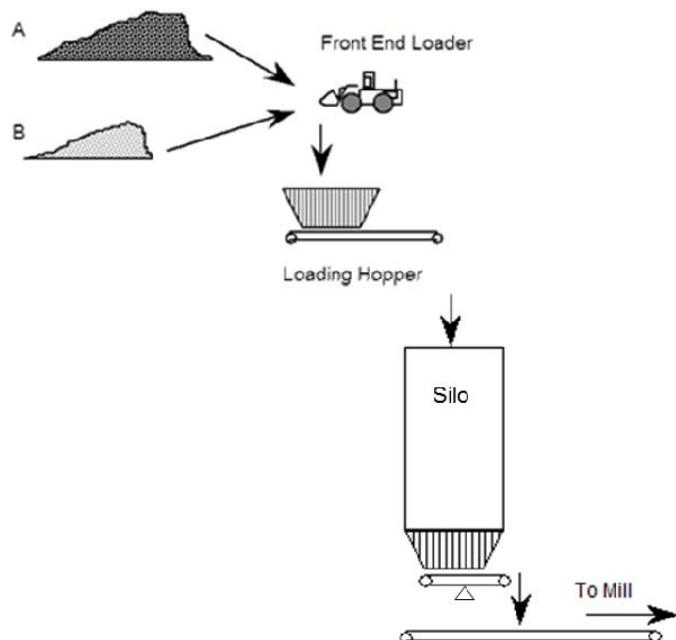


Figure 20: Blending of coal and petcoke via front-end loader

#### Advantages:

- Low cost solution
- Suitable for existing operations with only one silo

#### Disadvantages:

- Poor blending of coal and petcoke
- Only volumetric proportioning of coal and petcoke (subject to influenced by different FEL operators)

No real blending as essentially silo is filled in layers.

#### 8.1.2.2 Solution with **one** raw fuel silo and **two** feed points to the silo only (Semi-standard solution)

In this method separate loading hoppers are used for coal and petcoke. Blending is achieved through continuous volumetric extraction from the hoppers (or gravimetric extraction via optional belt scales) via common belt conveyor feeding to the raw fuel silo. After grinding the mixture of coal and petcoke is stored in respective bins for kiln and calciner.

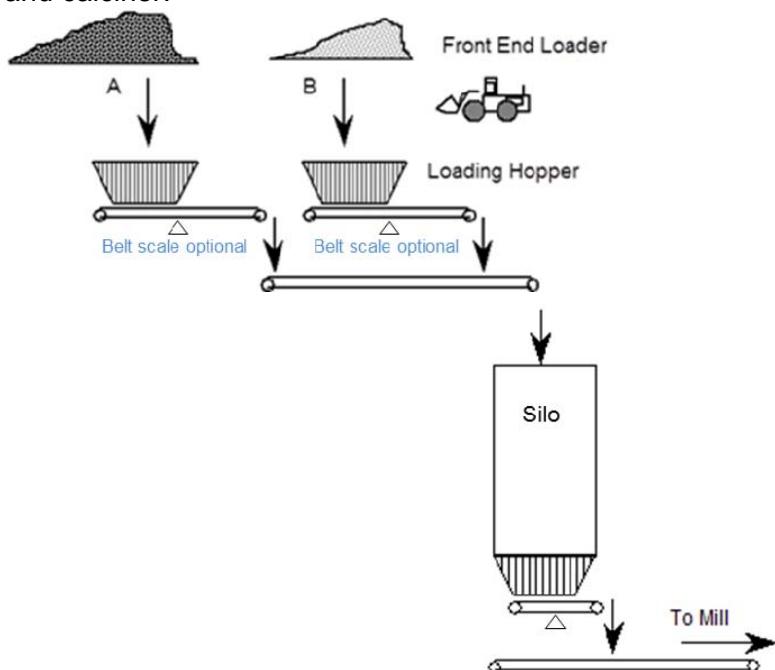


Figure 21: Blending of coal and petcoke via individual hoppers

##### Advantages:

- Better accuracy and blending efficiency compared to the one-hopper solution
- Blending ratio can be easily changed

##### Disadvantages:

- FEL operator must fill up both hoppers almost simultaneously which may be challenging as hopper capacity is generally small
- Different mixtures for calciner and main burner are difficult to manage
- Changing the ratio is only possible after emptying the raw fuel silo.

#### 8.1.2.3 Standard solution with two independent raw fuel silos

This concept comprises of one loading hopper with two silos. Only one silo is filled up at any given point in time. Accurate blending is achieved through continuous gravimetric extraction from each silo.

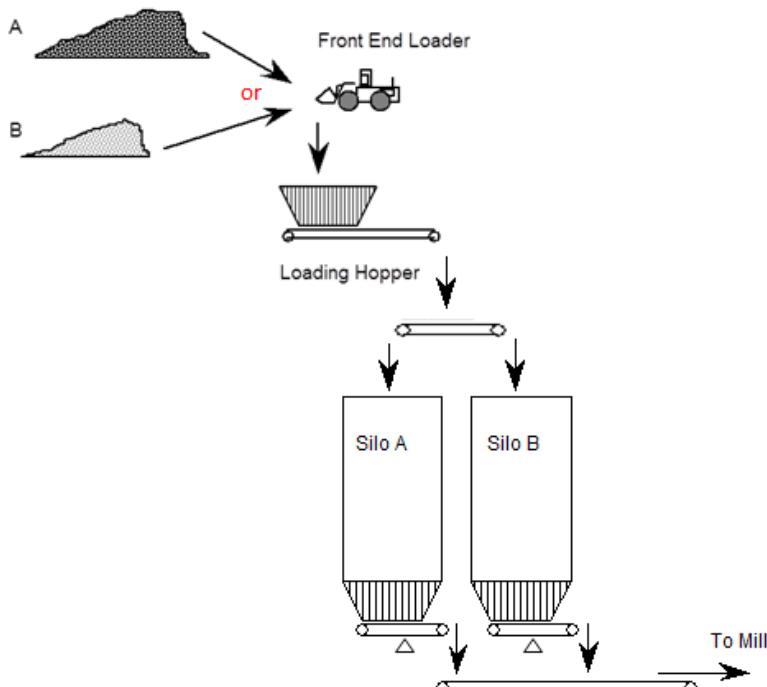


Figure 22: Blending of coal and petcoke with individual silos

#### Advantages:

- Accurate gravimetric blending of coal and petcoke ratio
- Blending ratio can easily be changed via weigh feeders enabling different blends for main burner and calciner).

#### Disadvantages:

- Capex required for a second raw fuel silo including dosing unit.

### 8.1.3 Dosing and transport to burners

The following table lists out some of the parameters for solid fuels. All other parameters are same as for pulverized bituminous coal (please refer to ‘Standard Design Criteria’ for further information).

Parameter	Petcoke	Anthracite	Bituminous coal	Lignite
Injection velocity, m/s	20-25	20-25	~30	30-40
Transport velocity, m/s	28-35	28-35	28-35	28-35
Dust concentration, kg/m <sup>3</sup>	3-5	1.5-2	5-7	5-7

### 8.1.4 Explosion protection

Due to the low volatile matter content it is easier to handle petcoke from safety point of view. Though petcoke is less reactive than coal, there are no different, less strict safety related guidelines for petcoke handling and grinding. Therefore a mill grinding petcoke or a mix of coal and petcoke must also follow all safety guidelines for coal grinding.

## **8.2 Grinding characteristics**

### **8.2.1 Grindability**

The grindability of petcoke and coal is indicated by the Hardgrove index (HGI). The lower the value, the harder is the material to grind. Coal has an HGI of about 50 °HGI. Typically the Hardgrove index of petcoke is lower than coal meaning that petcoke is harder to grind. Hence replacing coal by petcoke usually reduces production rate of the coal mill.

Anyhow, the Hardgrove Indices of petcoke from different origins can vary in the range of 30 to 70 °HGI.

### **8.2.2 Net calorific value**

In order to supply the same amount of thermal energy compared to coal less petcoke tonnage has to be ground. Hence lower production rates when grinding petcoke can be compensated to a certain extent by the higher NCV of petcoke.

### **8.2.3 Product fineness**

The required fineness for petcoke depends on its volatile matters (VM). The lower the volatile content, the higher the required product fineness. As petcoke has typically less volatiles than coal petcoke it has to be ground finer than normal coal reducing the coal mill production rate.

The fineness targets for 100 % petcoke are ideally:

$$\begin{aligned} R 90 \mu\text{m} &< 3 \% \\ R 200 \mu\text{m} &< 1 \% \end{aligned}$$

For co-grinding with coal the first approach requires 50 % of the average VM as residue on 90 $\mu\text{m}$ . That means for example a mix of 25 % petcoke with 10 % VM and 75 % coal with 30 % VM requires

$$R 90\mu\text{m} = \frac{1}{2} \times (0.25 \times 10 + 0.75 \times 30) = 12.5 \% R 90\mu\text{m}.$$

Finally the observation of the flame and the clinker quality is relevant for the necessary petcoke/coal fineness.

Achieved fineness in various Holcim plants are given in Figure 23 below where the red line shows the average value. It must be mentioned that especially the coarser fineness values are not intended but a consequence of the lacking grinding capacity or a consequence of the mixture with coal.

## 8.2.4 Petcoke moisture

Petcoke typically is received at lower moisture levels than coal. The lower the moisture content of the mill feed material, lower is the required drying capacity of the mill system. Therefore for petcoke grinding drying capacity is usually not a bottleneck. Typical values of moisture content range from 2-12 %.

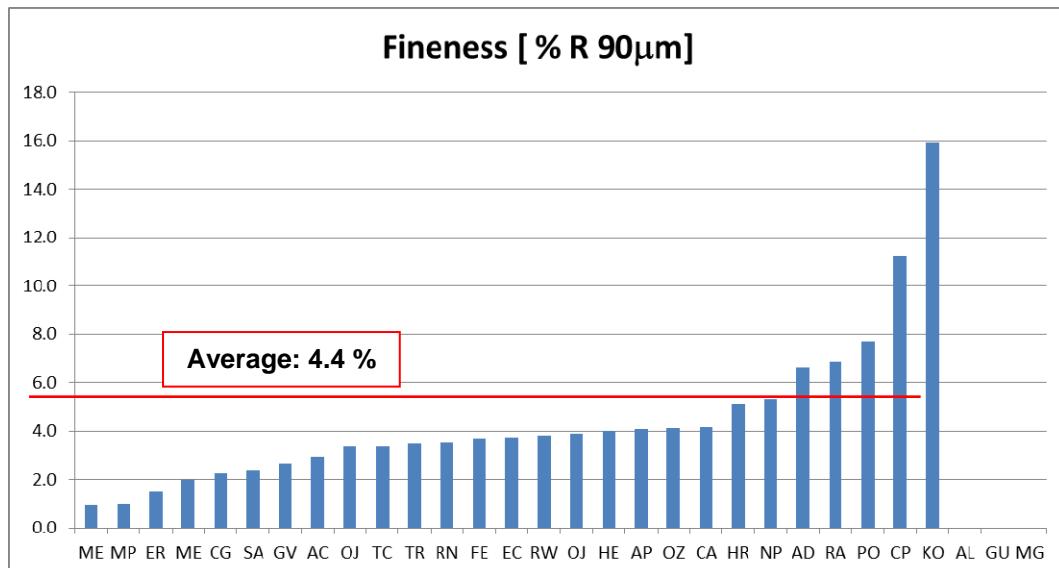


Figure 23: Petcoke fineness achieved at Holcim plants using >10 % petcoke total thermal energy (ATR 2012)

## 8.3 Grinding Systems

### 8.3.1 Petcoke grinding with vertical roller mills

The vertical roller mill (VRM) for petcoke grinding is usually able to grind both petcoke and coal. It must be dimensioned for the higher mass flow of low calorific coal and the harder and finer to grind petcoke. For this reason a VFD for the VRM drive is a standard solution for new coal mills.

Beyond that a VRM for petcoke must have a high efficiency separator with guide vanes and a cylindrical rotor cage of > 35 m/s circumferential speed in order to achieve the necessary fineness.

### 8.3.1.1 Petcoke grinding with VRMs in Holcim plants

Based on the ATR data Holcim plant utilizing VRM for petcoke grinding have reported production rates as shown below ranging from 4 – 34 t/h.

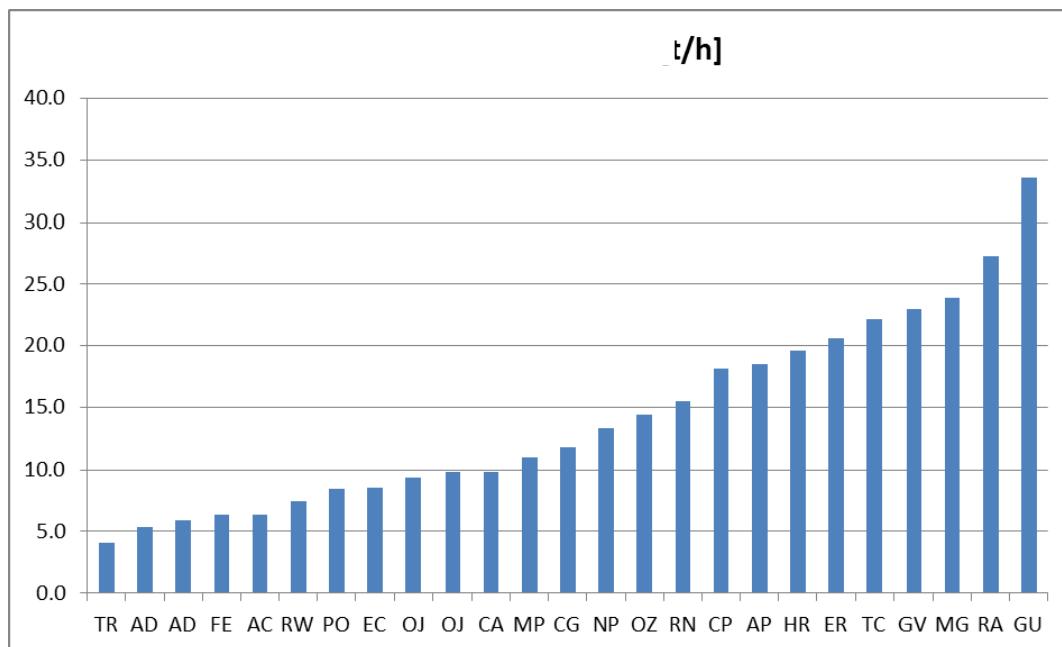


Figure 24: VRM production rate for petcoke grinding at Holcim plants (ATR 2012)

Mill motor specific electrical energy consumption (SEEC) and absorbed power from various Holcim plants are also given in the following figures.

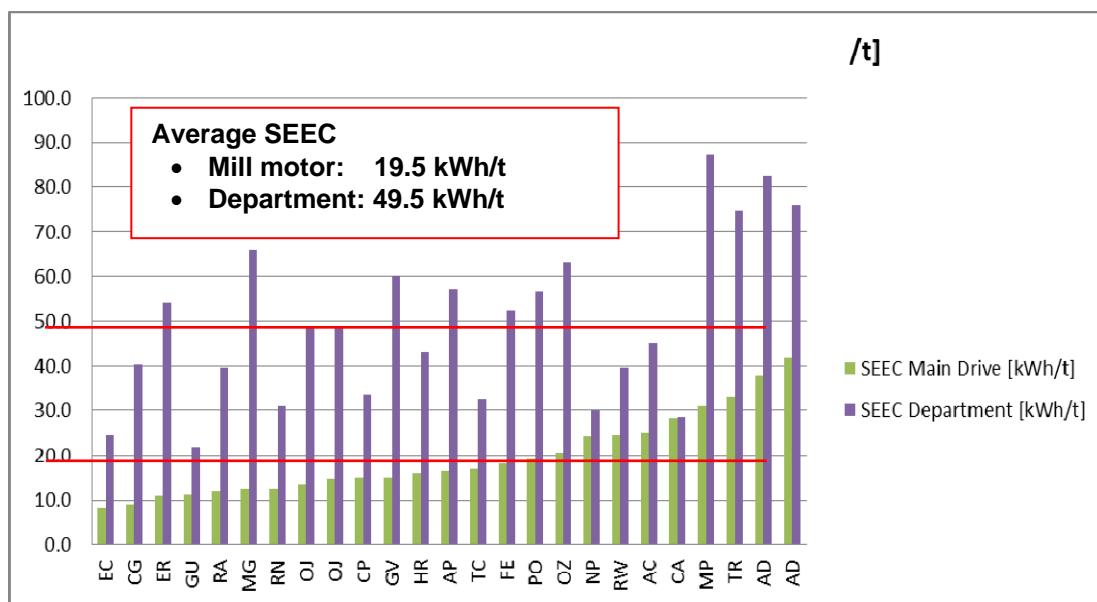


Figure 25: Specific electrical energy consumption (SEEC) of VRMs at mill motor and department for petcoke grinding at Holcim plants (ATR 2012)

### **8.3.2 Petcoke grinding with air swept ball mills**

In case of realizing that the VRM is unable to achieve the necessary grinding results in terms of fineness or capacity a ball mill is another option to grind petcoke.

Ball mill used for petcoke grinding must be air-swept mills without any bucket elevator for material transport. All ball mills for petcoke must be equipped with a high efficiency separator with sufficient rotor speed to achieve the desired fineness. Cement mills with mill discharge bucket elevators should not be converted to petcoke grinding mills due to safety hazards. A schematic of the ball mill for petcoke grinding is shown in figure below.

#### **8.3.2.1 Ball mills - Petcoke grinding in Holcim plants**

Data for the six Holcim air-swept ball mills for petcoke grinding are shown below for production rates, specific electrical energy consumption and mill motor absorbed power at counters in the following figures.

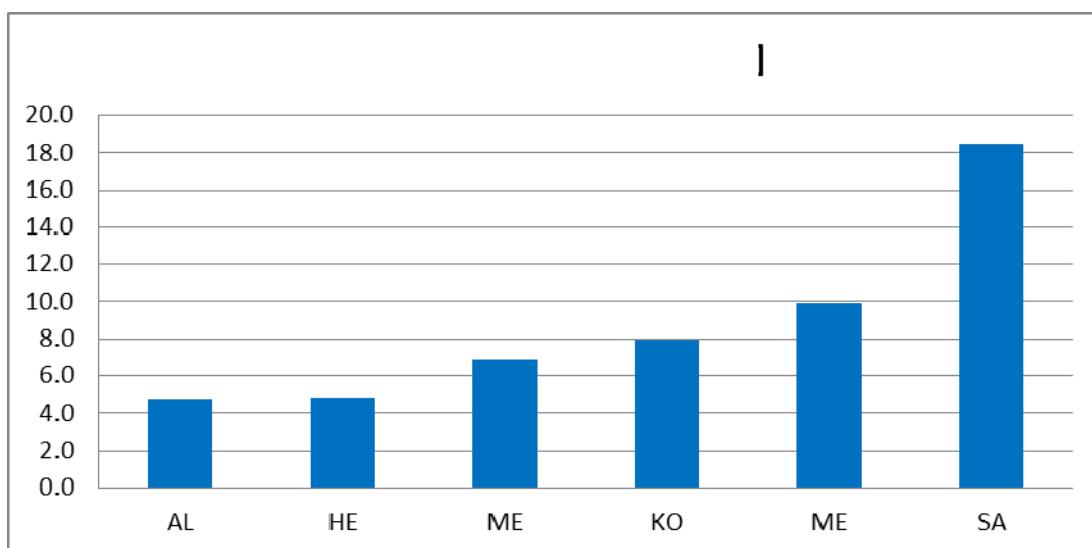


Figure 26: ASM production rates for petcoke grinding at Holcim plants (ATR 2012)

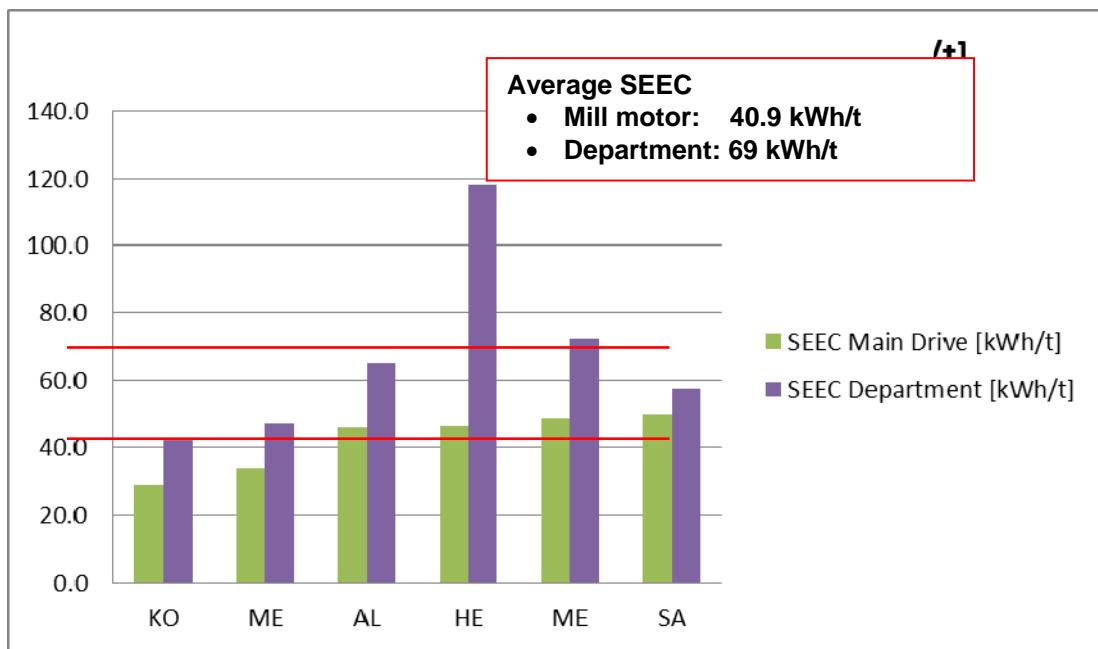


Figure 27: Specific electrical energy consumption of ASM (mill motor only and department) for petcoke grinding at Holcim plants (ATR 2012)

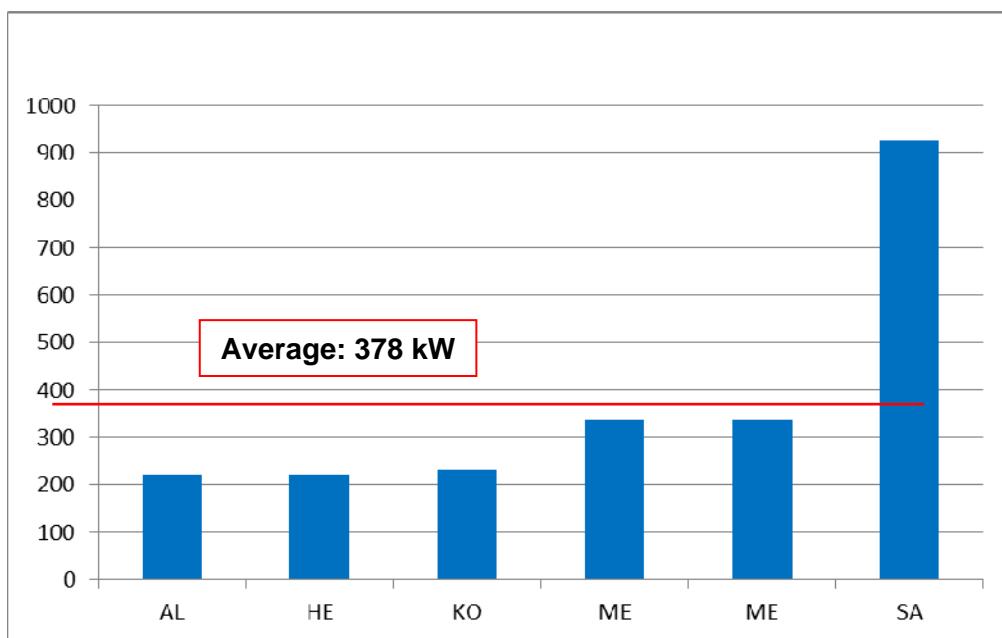


Figure 28: Absorbed power of ball mill (mill motor only) for petcoke grinding at Holcim plants (ATR 2012)

The majority of the ASM are small units of < 10 t/h capacity. SEEC with 40 kWh/t is double as high as for VRMs.

### 8.3.3 Recommended grinding system

Experience within Holcim plants using both VRMs and ball mills for petcoke grinding shows that vertical roller mills are the preferred choice due to lower specific electrical energy consumption and due to high flexibility of adjustment to plant needs in terms of production rate.

Petcoke like shot coke may be difficult to grind with VRMs. Only in case that the expected petcoke is difficult to grind in VRMs the ball mill may become the preferred solution. Settat and the expansion Barroso are examples where air-swept ball mills have been chosen as coal mills. In both cases this expected petcoke type was the reason for choosing ASMs for those new projects.

Polysius compared grinding coal/petcoke with different Hardgrove indices by grinding them both in a VRM and an air-swept ball mill. As expected the result represented in Figure below shows lower specific electrical energy for main motor and mill fan in case of a VRM. This advantage increases with harder coal.

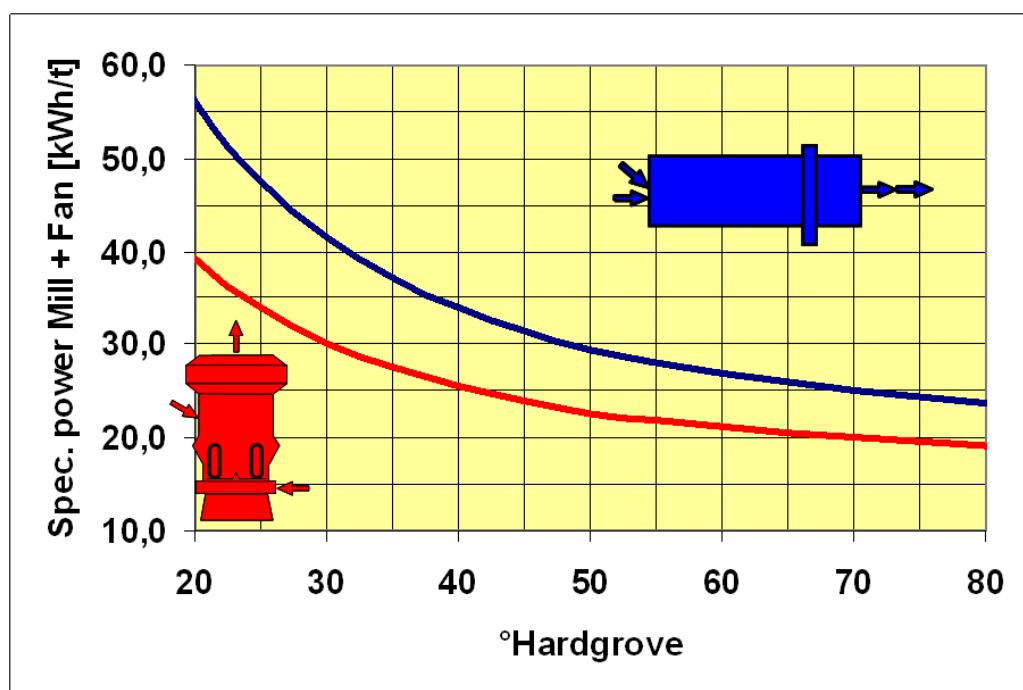


Figure 29: Specific electrical energy of mill main drive plus mill fan versus Hardgrove index in VRM and BM at 5% R90 µm (Source: Polysius)

## 8.4

### **Switch from coal to petcoke grinding**

For economic reasons plants with existing coal mills decide to introduce petcoke. In this case they have to switch to petcoke grinding or grinding a mixture of petcoke and coal. The following chapter describes the necessary and possible actions to be initiated in order to provide an acceptable fine petcoke in terms of quantity and quality.

#### 8.4.1

##### **Vertical roller mill**

Due to petcoke properties the friction factor between the rollers and the table is lower than it can be achieved with coal. Petcoke has the tendency of squeezing away during the grinding process. Hence the absorbable power of a VRM grinding petcoke is less than grinding coal at same grinding pressure. A first approach for estimating the absorbable power for pure petcoke grinding uses only 80 % of the regularly absorbed power during coal grinding.

The absorbable power of a VRM can be increased by certain measures:

- Central feed chute as close as possible to the mill table (if not already done)
- More accurate rejects chute as close as possible to the table
- More precise water injection below each roller
- Increased dam ring height
- VFD for the table drive to operate the mill at reduced table speed.

Only few documented cases in order to illustrate the statements are available.

In 2009 Saraburi 3 started to grind petcoke with the coal mill 2 (ATOX 27.5). Extending the feed chute as far as possible to the centre of the table and increasing of dam ring height from 165 mm to 195 mm was not sufficient to achieve a stable grinding process. Finally a significant reduction of the table speed to 80 % of the previous nominal speed was the key for success. The main process data are summarized in Figure 30 below.

Petcoke grinding Trials 25/07/2009						
Time		09:55	10:20	10:33	10:45	10:55
working pressure	[bar]	98	100	105	105	108
table speed *	[%]	75	75	80	80	80
classifier speed **	[%]	97	97	97	97	97
mill power	[kW]	390	410	455	500	
fan power vibrations	[kW]	718	725	730	730	
vibrations	[mm/s]	1.1	1.1	<1.5	1.4	
$\Delta p$ mill	[mbar]	21.2	21.3	21	22.3	
Feed	[t/h]	45	49	52	54	
Temp. Mill Outlet	[°C]	74	75	74	74	
R90	[%]	2.03	2.05	1.92	2	
watter add	[m³/h]	7.5	7.5	7.5	7.5	7.5
Grinding Bed	[mm]	~60	~60	~60	~63	~60
Spec. Energy ***	[kWh/t]	27.07	25.41	24.9	24.81	
Spec. Grind. Energy	[kWh/t]	8.7	8.4	8.8	9.3	
* 100% = 990 rpm						
** 100% = 147 rpm						
*** classifier power estimated with 110 kW						
Mill stop due to overloaded screw below EP						

Figure 30: Process data of the petcoke grinding test Saraburi 3 (Source: Report MPT 09/15808/E)

Another example is the plant Rabriyawas where the ATOX 22.5 was not suitable for petcoke grinding. After extending the feed chute, providing a water injection for each roller instead of one roller, removing the flap below the rejects chute and increasing the dam ring from 110 to 160 mm the mill was able to grind petcoke.

#### 8.4.2 Estimation of specific electrical energy consumption (SEEC), absorbable power and production rate of a VRM

In order to do a first estimation when switching from coal to petcoke following procedure can be used for calculating the expected results for a VRM:

- Calculation of the SEEC based on HGI, target fineness, water evaporation and partial load factor
- Estimation of the new absorbed power main drive
- Calculation of the mill production rate by dividing the estimated absorbed motor power by the calculated SEEC.

##### 8.4.2.1 Calculation of the SEEC

The coal grindability estimation sheet is a tool developed by HTEC based on the calculation of Loesche and own experience. Input data as shown in Figure 31 are:

- The composition of the expected petcoke/coal mix
- The HGI of the expected petcoke and coal types
- The differential water evaporation ( $\Delta H_2O$ ) meaning the difference of moisture in the raw coal/petcoke mix and the fine coal/petcoke

- The partial load factor meaning the utilization of the mill capacity. In case of calculating capacities this value should always be 100 %.

In the background of the spreadsheet calculation are several empiric curves representing the material and VRM behaviour depending on the input values. Final result in the last line is the expected SEEC at mill motor shaft ( $E_{\text{spec mill}}$ ). In the example Figure below it is 15.7 kWh/t with an HGI of 38.

Coal grindability estimation			
Plant:	Darlaghat	Date:	01.05.2007
Mill Nr:	Coal Mill 1	Visa:	BAT
Coal / petcoke type	Petcoke		
Coal / petcoke mix	100 [%] Type 1 0 [%] Type 2 0 [%] Type 3	38 [°H] 50 [°H] 60 [°H]	
Average Hardgrove Index	38 [°H]		
Product R90 $\mu$ m	5 [%]		
Delta H <sub>2</sub> O	5 [%]		
Partial load factor	100 [%]		
E spec mill (motor shaft)	15.74 [kWh/t]		

Figure 31: Example for input values for 100% petcoke

For the detailed calculation the entire program must be adjusted with real case audits of known coal HGI.

#### 8.4.2.2 Estimation of the absorbed power of the mill drive

The new absorbable power at mill drive can only be estimated based on the previous operation. In case of switching from 100 % coal to 100 % petcoke the new absorbable power can be estimated with 80 % of the previously absorbed power. In case of just increasing petcoke percentage a factor > 80 % can be assumed.

In case of having previously 460 kW absorbed with 100 % coal switching to 100 % petcoke will reduce absorbed power probably to  $460 \text{ kW} \times 0.8 = 370 \text{ kW}$ .

#### 8.4.2.3 Calculation of the mill production rate

The expected production rate can be calculated by dividing the absorbable mill motor power by the calculated grindability. In the example it would be

$$370 \text{ kW} / 15.7 \text{ kWh/t} = 24 \text{ t/h}$$

#### 8.4.3 Air-swept ball mill

Using an air-swept ball mill for petcoke grinding doesn't require significant modifications as long as the separator is a rotor cage separator with > 35 m/s circumferential speed. In case the mill is not fully charged with balls it should be topped up with maximum ball charge in order to have maximum output.

#### 8.4.3.1 Estimation of specific electrical energy consumption (SEEC) and production rate of an air-swept ball mill

When switching from coal to petcoke following procedure can be used for calculating the expected results for a ball mill:

- Calculation of the SEEC base on HGI, target fineness and water evaporation and partial load factor.
- Calculation of the mill production rate by dividing the estimated absorbed motor power by the calculated SEEC.

Same procedure for the calculation of the expected grindability can be applied for the ball mill. As the spreadsheet is designed for VRMs the result has to be multiplied with a conversion factor of 2.0 in order to get the necessary grindability for the ball mill drive. That means in our example the expected SEEC at ball mill motor shaft will be

$$15.7 \text{ kWh/t} \times 2 = 31.4 \text{ kWh/t.}$$

The absorbed power of a ball mill depends on the mill dimensions and the ball charge filling degree. A simplified approach is that the absorbed power of a ball mill is constant and independent of the coal or petcoke type.

Hence finally the absorbed power can be divided by the SEEC<sub>ball mill</sub>. Assuming constant 500 kW of the ball mill the new production rate would be

$$500 \text{ kW} / 31.4 \text{ kWh/t} = 16 \text{ t/h.}$$

## 9.

### **PETCOKE COMBUSTION**

In a simplified model, solid fuel combustion may be visualized as consisting of three consecutive reactions:

1. De-volatilization and ignition of the volatile matter
2. Combustion of the released volatile matter in gas phase
3. Combustion of the residual char at the particle surface

While the first two reactions take place at a rapid pace (usually in the range of milliseconds), char-burnout requires several seconds. The low reactivity of petcoke has an influence on the first and third reaction. The low volatile matter content in petcoke makes it more difficult to ignite compared to coal. Furthermore, petcoke combustion produces a less porous char (lower specific surface area) which increases the time required for char-burnout. These effects need to be compensated by adjustments of the kiln operation as well as by grinding the petcoke finer.

The key factor for successful petcoke utilization is a good control of the sulfur volatilization in the kiln system, which is strongly influenced by the completeness of combustion in the main firing, secondary firing as well as in the calciner firing. In order to achieve complete combustion, the following ingredients are essential:

- sufficient **Temperature**
- sufficient **Oxygen**
- sufficient **Time**
- sufficient **Mixing**
- sufficient **Fineness**

Complete combustion is mainly characterized by CO levels < 0.05% or 500 ppm (max. 0.1% or 1'000 ppm) at the kiln inlet and pre-calculator exit. Another indication for incomplete burnout in the secondary or pre-calculator firing is an increased level of unburnt organic carbon in the hot meal of the bottom stage cyclone. Usually sparkling of the hot meal sample when in contact with ambient air is a first indication. But hot meal can also be analyzed for TOC with a carbon analyzer e.g. Leco.

## 9.1

### **Main firing**

In order to ensure a complete combustion at the main firing of the kiln, the following needs to be considered.

Sufficiently high **temperature** is needed in order to ensure faster ignition. Therefore, a stable cooler operation with a high secondary air temperature is required. Additionally a high burner momentum ensures external recirculation of hot kiln gases and fast mixing between the fuel and air. The delayed ignition behavior of petcoke, leading to a longer black plume at the root of the flame can be compensated by lower injection velocity of the petcoke (20-25 m/s) compared to coal (25-30 m/s).

In order to ensure complete combustion of petcoke, higher kiln inlet **oxygen** is required. For 100% petcoke utilization the oxygen typically needs to be increased by approx. 1% compared to normal coal firing. Therefore a reliable gas analysis at the kiln inlet is imperative in order to control the oxygen level.

Higher gas velocities due to the higher oxygen demand and the slower burnout of petcoke tend to elongate the main flame and create a flat temperature profile in the kiln. In order to counter act this tendency the momentum of the main burner needs to be increased to improve **mixing** between the fuel and combustion air. The flame needs to be adjusted as short and hot as possible, up to the limit where an overheating of the kiln shell would occur. A short flame does not only help to improve burnout but exposes the material charge in the kiln only for a short time to high temperatures.

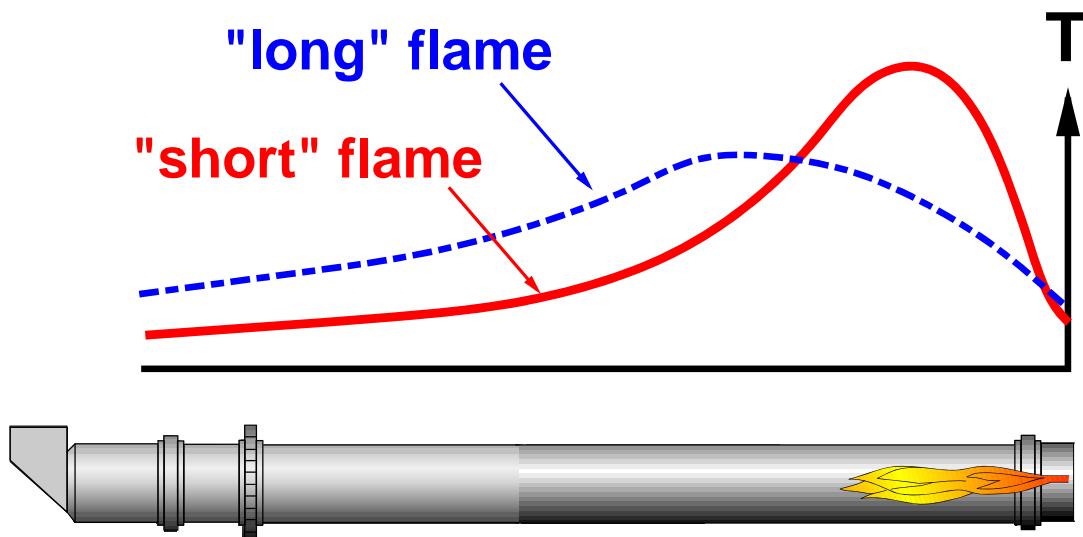


Figure 32: Flame length vs. flame temperature

The main burner operating parameters for petcoke can be summarized as:

- Specific burner momentum = 9-11 N/MW
- Primary air fan pressure > 250-300 mbar
- Primary air ratio = 13-15% (based on stoichiometric combustion air, excluding transport air)
- Alignment of burner with the axis of the kiln

Residence **time** is usually not a critical factor in the main firing as long as the other key parameters (temperature, oxygen, mixing and fuel fineness) are well controlled. New kilns specifically designed for high petcoke and AFR use should have three supports and a length:diameter ratio of approx. 15, corresponding to a gas residence time in the rotary kiln of > 9 seconds.

In order to compensate for the lower volatile matter content and therefore more difficult ignition and burnout behavior of petcoke, it needs to be ground finer. The increased **fineness** also helps to prevent dropping of unburnt fuel particles on to the material bed. Unburnt fuel drop out may lead to local reducing conditions which in turn promote sulfur volatilization. The recommended fineness targets are provided in the section 7.2.3

Blending and/or co-grinding of petcoke with a high volatile coal (e.g. lignite) should be avoided. The two fuel types have typically exactly opposite combustion and grinding behavior. The rather soft lignite gets over-ground, while hard petcoke enriches the coarser fraction of the ground fuel. Furthermore the flame is very difficult to control. Grinding petcoke and lignite separately and dosing of the two fuels from separate fine fuel bins could be a possibility to overcome such a limitation.

## 9.2

### Pre-calciner

Achieving complete combustion with petcoke in the pre-calciner can be challenging, especially as pre-calciners are operated at temperatures between 850-900°C. Therefore special means need to be foreseen in pre-calciners to ensure good ignition and burnout of less reactive fuels such as petcoke.

It is crucial to maintain a higher **oxygen** level to ensure CO remains below 0.05% (500 ppm). Compared to normal coal firing the oxygen level at the pre-calciner exit needs to be increased, typically 1% increase in oxygen for 100% petcoke.

Another indication for incomplete burnout in the calciner is an increased level of organic carbon in the hot meal of the bottom stage cyclone (if TOC > 0.1%). Usually sparkling of the hot meal sample when in contact with ambient air is a first indication. But hot meal can also be analyzed for TOC with a carbon analyzer (e.g. Leco).

The fuel ignition can be considerably improved by increasing the **temperature** in the region where fuel ignites, from 850-900°C to 1000-1100°C by creating a "Hot Spot" (Figure 33). A calciner equipped with a "Hot Spot" contains a hot region in the lower part of the calciner to facilitate the fuel ignition. By locally reducing the addition of the uncalcined meal in this region, less heat is absorbed by the endothermic calcination reaction and hence the gas temperature goes up.

The upper limit of achievable temperature in the ignition zone is usually limited either by the formation of buildups (onset of liquid phase formation, molten ash) or by local overheating of the calciner vessel.

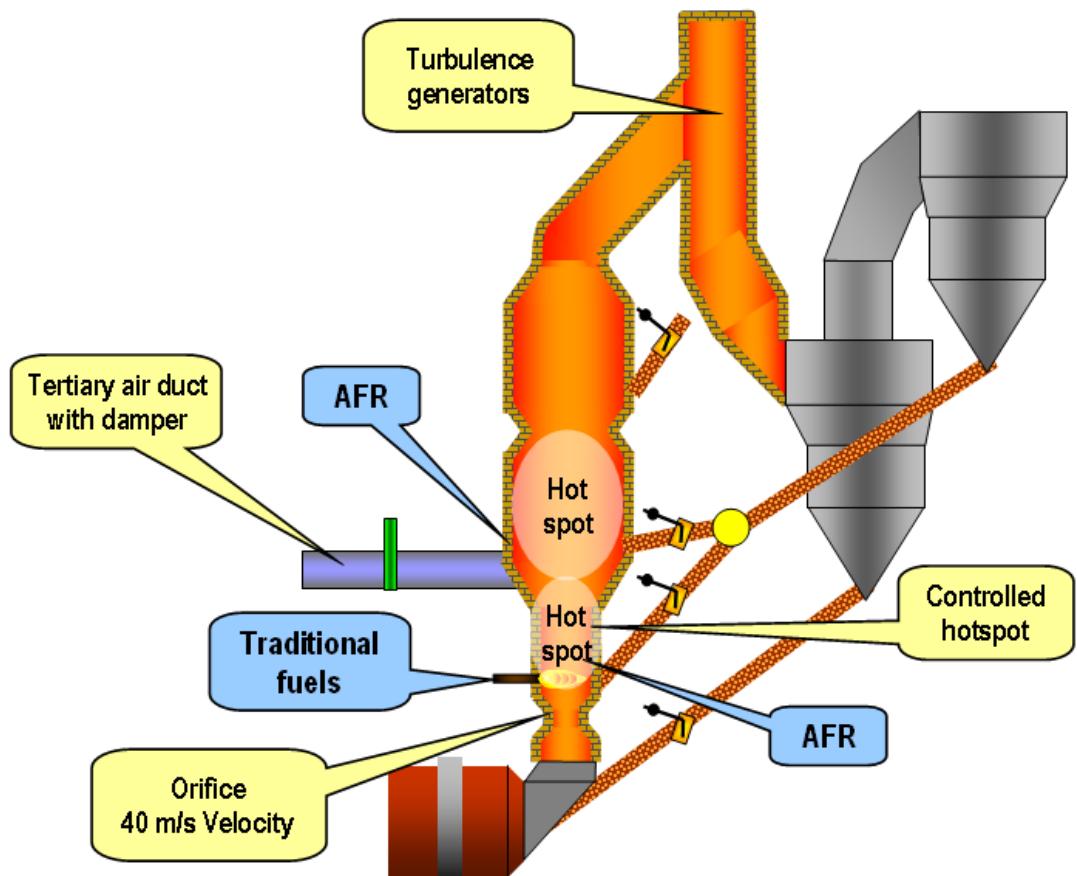


Figure 33: Formation of “hot spot” in the pre-calciner

A controlled “hot spot” is created by installing an additional meal feed point downstream of the calciner and splitting the meal from the second lowest cyclone to the two feed points. Careful observation of the temperature of the “hot spot” region is important to prevent local overheating which may lead to premature refractory failure, burner tip damage, localized clinkering or formation of hard buildups. In the so-called controlled “hot spot”, an automatic control loop could be useful to maintain the desired temperature of the hot zone by adjusting the meal splitter gate position.

An even better ignition and burnout behavior for petcoke can be achieved in calciners with pre-combustion chamber (PCC). In a PCC (Figure 34), the ignition takes place in a hot flame ( $1600^{\circ}\text{C}$ ) together with pure (21%  $\text{O}_2$ ) and hot tertiary air. Furthermore, the combustion in a PCC takes place without any negative impact from rotary kiln exhaust gases and without any cooling effect of endothermic decarbonization reaction of the raw meal. This altogether ensures good ignition and combustion conditions to achieve 100% burnout of petcoke.

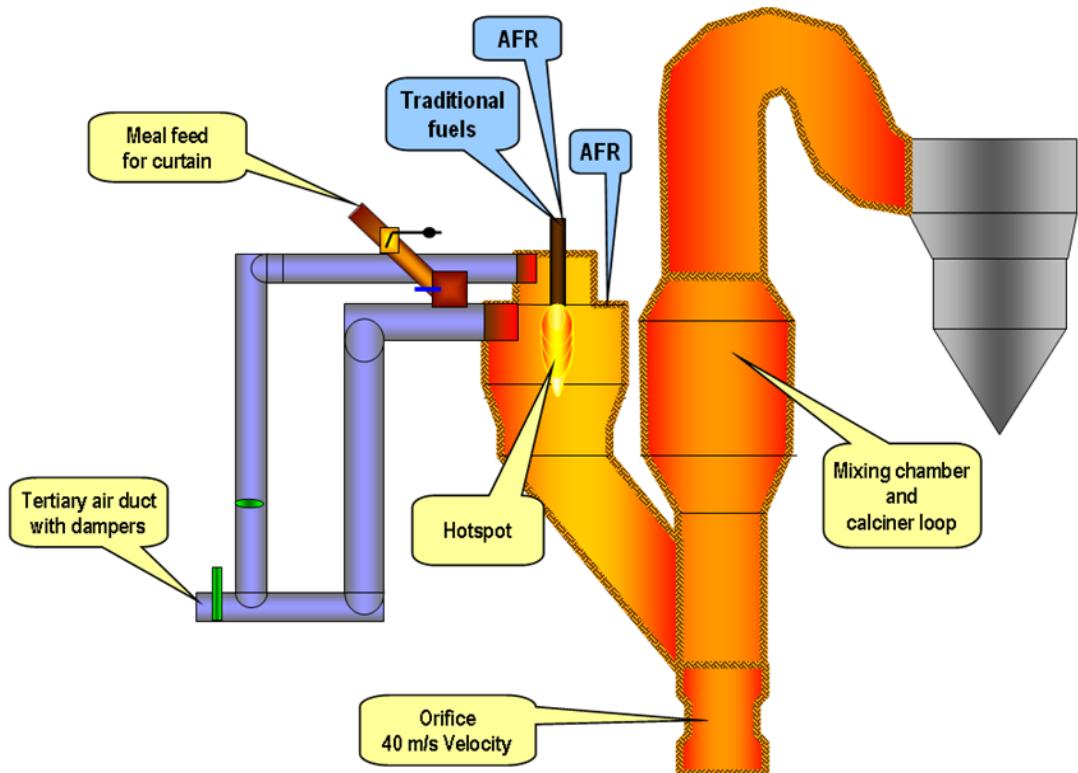


Figure 34: Typical set-up of a pre-combustion chamber (PCC)

Besides oxygen level and temperature, gas retention time in the calciner is a decisive factor for complete burnout of the petcoke. For the new pre-calciners, HTEC Standard Design Criteria (StDC) recommends the following,

Fuel	Gas residence time, s	
	In-line calciners	Separate line calciners
Petcoke	4	3
Bituminous coal	3	2
Lignite	3.5	2.5

However, achieving complete combustion of petcoke in older pre-calciners (with lower gas residence time) can be a big challenge. In absence of a major modification e.g. enlargement of the calciner, the improvement potential should be focused on the optimization of the other key parameters (oxygen level, temperature, petcoke fineness).

In certain cases, a different arrangement of the petcoke burners (e.g. relocation of the burners further towards the kiln orifice or cross-current downward alignment of burners) has improved the situation.

Another option to improve the burnout in an existing installation is the optimization of the mixing between the fuel and air. This can be achieved by addition of primary air (e.g. swirl) to the petcoke burners, installing additional turbulence generators in the calciner vessel or modification of the tertiary air inlet. It is important that, due to the different designs of pre-calciners, each installation should be evaluated on case by case basis to identify the most suitable optimization measures.

The guide value of the petcoke fineness for the pre-calciners is the same as for the main firing. Nevertheless in several cases of older type calciners with low residence time, a finer fuel improved the combustion conditions.

### 9.3

#### **Petcoke and AFR**

Several plants in the Holcim group have achieved 100% petcoke together with AFR firing. Nevertheless a few important interactions between AFR and petcoke need to be considered to make it work.

The use of high-grade liquid AFRs ( $NCV > 20 \text{ MJ/kg}$ ) creates typically no problem if the correct atomization nozzle is used with the right amount and pressure of compressed air. They even support the ignition of the petcoke at the main firing.

High inputs of chlorine, often from AFR lead to the formation of a chlorine cycle in the kiln, which also contributes to build-up formation in the preheater tower. High chlorine inputs therefore reduce the ability to also have, at the same time, high sulfur levels in the hot meal and thus high sulfur inputs to the kiln.

When firing fine solid AFRs (3-dimensional solids  $< 5 \text{ mm}$  incl. 2-dimensional foils  $< 50\text{mm}$ ) at the main firing together with petcoke, it is essential to prepare them fine enough. If solid AFRs fed to the main burner contain significant amount of 3-dimensional solids  $> 5 \text{ mm}$ , this fraction will drop-out on the material bed before being completely burnt out and increase the sulfur volatilization by creation of local reducing conditions.

Furthermore, the use of lumpy AFRs (e.g. whole tires) at the secondary firing (kiln inlet) has resulted in many cases to an increased sulfur volatility. Lump fuels cannot be suspended by the kiln gases and hence burn on the material bed in the back end of the rotary kiln, creating local reducing conditions.

Another factor that can impact sulfur volatilization significantly is the use of coarse solid AFRs (3-dimensional solids  $< 50 \text{ mm}$  incl. 2-dimensional foils  $< 200\text{mm}$ ) in inline calciners. If the solids fed to the pre-calculator are too large or the calculator orifice velocity is not high enough (should be  $\geq 40 \text{ m/s}$ ), these material will not remain suspended in the calculator vessel. In the end, the unburnt material will fall through into the kiln inlet chamber and enhance the sulfur cycle in the kiln.

### 9.4

#### **Kiln preheating and start up**

During kiln preheating and start up, the use of petcoke requires multiple changes. Due to the more difficult ignition behavior of the petcoke, the transition of heavy fuel oil/ diesel or gas during the heat up will be later than when using coal.

The exact transition period depends on the petcoke fineness and quality and for this reason; no general recommendation is made here. Typically the transition to petcoke will be started approx. 12-18 h after the light up of the burner and ends 1-2 hours after the start-up of kiln feed (i.e. after hot clinker in the cooler). Some plants have reported to discontinue the use of startup fuel just before the kiln startup.

In absence of kiln feed during the heat up period,  $\text{SO}_2$  emissions will increase drastically due to the use of petcoke. For this reason, petcoke is generally not

recommended during heat up phase (before kiln start up). It is recommended to check local regulations carefully before using petcoke for kiln preheating.

In case the calciner is equipped with pre-combustion chamber (PCC), the kiln start-up becomes more difficult with 100% petcoke. For the kilns equipped with a PCC (e.g. RSP, CC chamber from Polysius, FLS SLC-D or FCB Calciner), self-ignition of petcoke ( $> 700^{\circ}\text{C}$ ) is not given since tertiary air temperature at PCC and SLC kilns are low during the startup phase. For this reason a startup fuel (heavy fuel oil, diesel or gas) is required to ensure safe ignition. The use of the fuel can be discontinued shortly after the startup, typically some hours after the first kiln feed.

In SLC kilns the use of startup fuel depends on the startup procedure. If the SLC is started only after the availability of hot tertiary air, it might be possible to ensure self-ignition of petcoke without a startup fuel. In case SLC is started shortly after the first kiln feed, use of startup fuel becomes necessary.

## **10. CHALLENGES IN USING PETCOKE**

### **10.1 Challenges - Electrical energy**

- In some cases, petcoke grinding results in higher specific electrical energy consumption (kWh/GJ) in comparison to coal.
- In certain cases, higher electrical energy consumption was reported also for cement grinding due to different micro-structure of the clinker formed with petcoke firing.
- A small increase in electrical energy consumption of the kiln section due to the increase of specific heat consumption.

### **10.2 Challenges - Thermal energy**

Thermal energy consumption goes up due to higher excess air requirement (1% O<sub>2</sub> increase for 100% petcoke). As a rule of thumb, +1% O<sub>2</sub> increase results in kiln heat consumption to increase by 1.8%<sup>1</sup>.

### **10.3 Challenges - Kiln capacity**

To burn petcoke, a higher excess air level is required to ensure complete combustion. As a rule of thumb, +1% O<sub>2</sub> increase required for 100% petcoke results in production loss of 5-6% (dry kilns) and 4-5% (wet kilns).

### **10.4 Challenges – Petcoke grinding capacity**

As petcoke has basically a higher grindability compared to coal coal mill production will drop. VRMs will also absorb less power compared to coal grinding due to a lower friction factor between rollers and table.

The range of production loss in terms of t/h depends on the previous coal type and the petcoke and will be in the range of 30 to 50%. Usually the loss is not compensated by the higher CV of petcoke compared to coal.

### **10.5 Challenges - Kiln operation**

With the increased input of sulfur from petcoke the situation regarding build-up and ring formation will become more critical, which can lead to a reduced availability of the kiln system.

Most important point for constant sulfur volatility is continuity in operation without drastic changes, which minimizes the fluctuations of the burning zone temperature. KilnMaster (or other high-level control system) can be helpful to improve the kiln stability.

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<sup>1</sup> Reflects heat increase if the stability of the kiln remains unaffected due to switch to 100% petcoke. In case of lower MTBF is encountered, > 1.8% heat increase should be expected!

Ring and build-up formation is clearly linked with sulfur volatilization and as such often an issue when using petcoke. Sulfur-spurrite,  $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_3$  or  $2\text{C}_2\text{S}\cdot\text{CaSO}_4$ , is formed by interaction of the  $\text{SO}_2$ -rich gas with belite and free lime.

The sulfur-spurrite forms long needles, which interweave with the meal and refractory walls to form low density rings and balls especially in long kilns. The location is typically before the upper transition zone. Additional material buildups are common in the riser duct and lower preheater cyclones also.

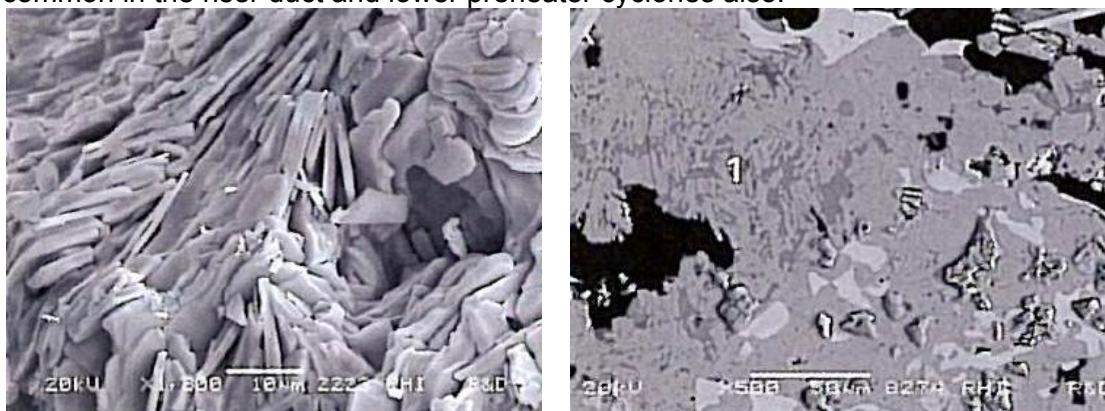


Figure 35: Plate-like crystals of sulfospurrite (left) as observed by scanning electron microscope; and in polished section, sulfospurrite indicated by "1" (right)

In order to reduce build-up formation and improve sulphur incorporation into the clinker, sulfur volatility needs to be well controlled. Furthermore the build-ups need to be managed.

To control and monitor the sulfur volatility, measurements on hot meal should be made. The frequency of sampling is determined by process requirements, but normally every 4 hours (or every 8 hours for problem-free kilns). Parameters to be measured on hot meal are:

- Loss on ignition
- $\text{SO}_3$
- Chlorine
- $\text{K}_2\text{O}$
- $\text{Na}_2\text{O}$

Note that measurement by XRF requires a separate calibration curve for hot meal analysis and that  $\text{SO}_3$  should be measured by LECO (which can also measure the carbon content).

Due to the high temperature and variable pressure, sampling of hot meal requires care and caution. Due to safety reasons, manual sampling of hot meal is discouraged. A design for a simple yet effective manually operated hot meal sampler is shown in Annex 5, with more detailed design available from HTEC/CM-QPC on request.

## 10.5.1 Build ups operative measures

### 10.5.1.1 Preheater Cleaning

Preheater cleaning needs to be intensified because of the higher inputs of circulating elements (sulfates, alkalis and chlorides). Regular manual cleaning must be avoided as much as possible to minimize the risk in this dangerous task. In the following sections, automated cleaning possibilities are extensively presented in order to reduce the exposure of cleaning personnel to hot material.

### 10.5.1.2 Detection

Based on the concentration of SO<sub>3</sub> and Cl in hot meal, Figure 18 (section 7.2) can be used to get the first information about build-up tendency. The limits shown in this graph are generic and need to be adapted to the local situation. There are a number of methods to detect the build-up formation and/or blockage of cyclones.

### 10.5.1.3 Detection of cleaning need

- Pressure measurements in the preheater tower, higher negative pressure show need for cleaning. Typically the pressure measurements at the kiln inlet, below above the orifice and intermediate locations before the lowest stage cyclone are the most used ones for the blockage detection.
- Regular timed cleaning 1-2/shift. The frequency is adapted according to the build-up situation the cleaning crew observes during cleaning.
- Cleaning frequency is adapted according to the concentrations of SO<sub>3</sub> and Cl in the hot meal.
- Typically a combination of pressure measurements and the observations of the cleaning crew will define the cleaning intensity.

### 10.5.1.4 Detection of cyclone blockages

This is typically installed in the lowest two to three stages of a preheater. Three different concepts exist:

#### ➤ **Gamma ray detection**

A gamma source is placed in the lower half of the cylindrical part of the cyclone. The receiver can also detect gradual increase in thickness of the build-ups. However, many countries require extensive permits for installation of such a device.

#### ➤ **Meal temperature measurement**

A pyrometer measures the meal temperature. A dip in the temperature indicates a cyclone blockage.

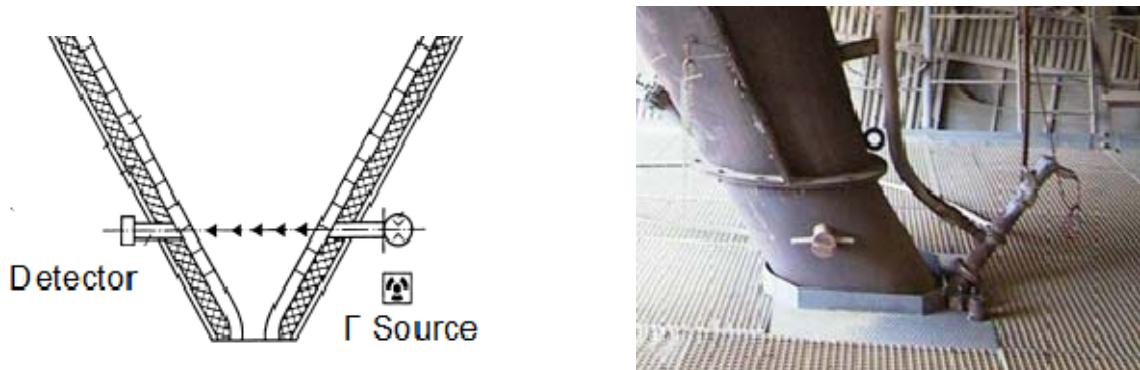
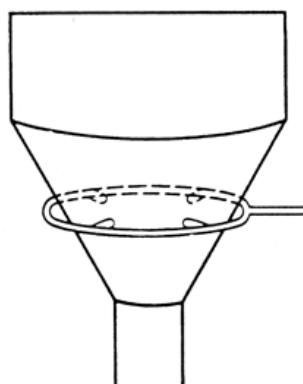


Figure 36: Gamma ray detection (left) and meal temperature measurement with a pyrometer with insulated air (right)

➤ **Pressure measurement in the cone of the cyclone**

Several openings on the cone of the cyclone are connected with a ring. A pressure transmitter measures the pressure in this ring. A blockage can be detected by different concepts:



One common point of all these concepts is that the pressure measurement ports itself could be blocked. For this reason, a system comprising of automatic cleaning with compressed air should be installed. The alarm is raised, if the situation doesn't improve after 2 cleaning cycles.

Figure 37: Pressure measurement in cone

No more fluctuations in the cone pressure

- $\Delta p$  cone to gas outlet cyclone
- $\Delta p$  cone to meal duct

As the cleaning procedure will delay the shutdown of kiln, there is a risk of increased material accumulation in case of a cyclone blockage.

The differential pressure measurement cone to cyclone gas outlet is the most common installation now-a-days.

#### 10.5.1.5 Access

**Kiln riser dust and orifice area:** Small cleaning doors used for regular cleaning need to be available in sufficient quantity. The big doors in the middle of the ducts are used for extraordinary cleaning while the kiln is in stop condition (and for maintenance activities in the annual shutdowns).

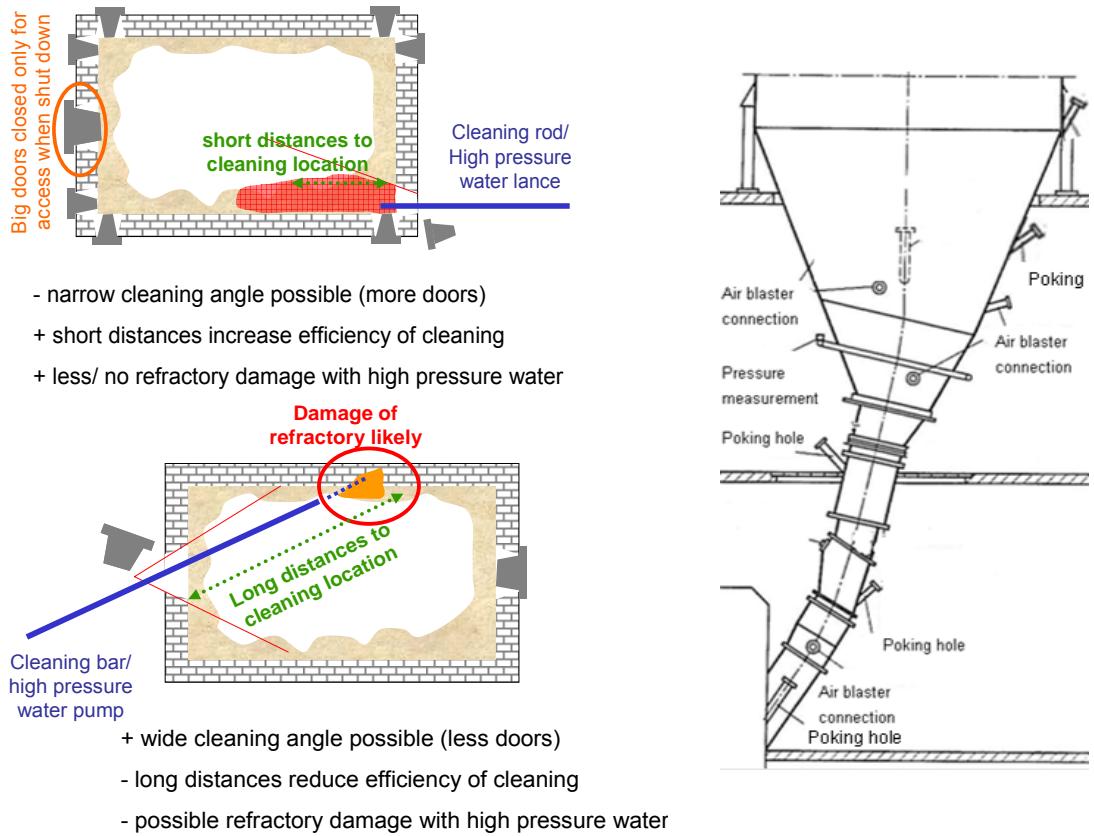


Figure 38: Accessibility of the cleaning doors (left: top & bottom) and cyclone poking holes (right)

**Cyclones:** Openings to clean the cyclones are located in the transition between the cylindrical and the conical part. In big cyclones, additional ports might be required. The splash box and the meal duct in the lower stages are typically equipped with some openings. Generally, the lowest stage meal ducts are equipped with the most cleaning possibilities.

It is important to check following points,

- Ease of opening and closing
- Air tightness
- Lockable when closed

The preference is doors which are easy to open. Figure 39 shows poking holes where a gravity-operated door closes (and locks) automatically due to gravity, while a horizontal door needs to be locked with a pin and chain.

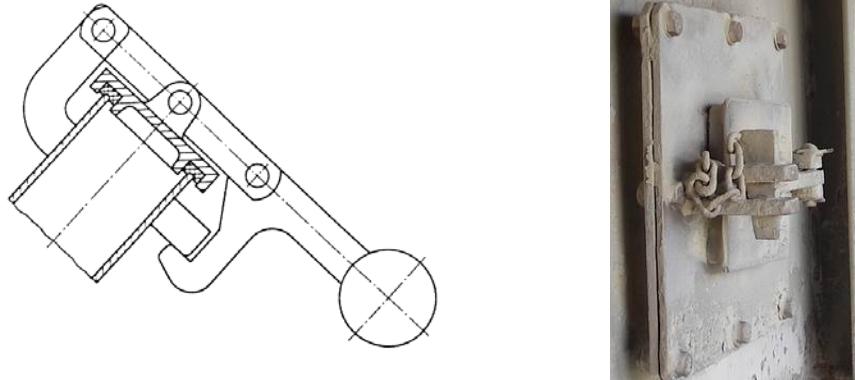


Figure 39: Poking hole cover: gravity-operated (left) and chain-operated (right). Exposure of personnel to the hot gases can be minimized with a ball valve that can be mounted on the open cleaning doors. The cleaning with these valves in place requires less PPE e.g. just a hard hat with face shield and neck protection (no need for complete hood). However, fully protective heat resistant clothing is required for the placement of the ball valve.



Figure 40: Ball valve arrangement

With the ball valve in place, cleaning can be performed in a safe way without standing directly in front of the door. Sufficient space/platform should be provided on either side of the door to ensure good accessibility. It is important to consider wind direction before selecting the cleaning location.

#### 10.5.1.6 Cleaning methods

Four types of cleaning can be performed:

- Manual with bars, air lances or jackhammers
- Air blasters
- ATD Cardox CO<sub>2</sub> blasting
- High pressure water cleaning

**Cleaning frequency:**

Normal shift cleaning is done as per the usual frequency. Based on the pressure drop across the preheater tower, additional cleaning should be ordered by the kiln operator.

**Safety:**

Automated (air blasters) or CARDUX systems are the preferred methods as these limit exposure of personnel to potentially dangerous situations. In situations where

manual cleaning has to be performed, appropriate personal protective clothing must be worn, even in hot climates!

For high pressure water and ATD Cardox cleaning, only the specially trained personnel should be allowed to operate the equipment.

#### 10.5.1.7 Cleaning tools

##### 10.5.1.7.1 Manual cleaning



Figure 41: Bar hammer (top left), Air lance (bottom right), Jack hammer (right top & bottom)

##### Critical points:

- Poking bars should be round not with edges.
- Air lances have to be equipped with a ball valve to allow dosing of the utility air
- All tools should allow to work >1 m outside of the opening
- Typically air lances are >4-6 m long
- Appropriate racks for storage of the cleaning tools minimizes risk of stumbling down
- Mixing of air and water (low pressure, <150 bar) or water alone (low pressure, <150 bar) will cause refractory damages and for this reason not recommended.

#### 10.5.1.8 Air blasters (or air cannons)

Air blasters are vessels filled with compressed air where the air is released in a very short timeframe creating a shock wave that cleans up the area around the nozzle.



Figure 42: Air blaster filling up (left) and setting off (right)

Most nozzles will be cast in the refractory lining. Since this will require refractory repairs for worn out nozzles, the following exchangeable nozzles can be utilized. They will allow changing nozzles within a short timeframe requiring no refractory adaptations after the base frame has been integrated in the refractory.

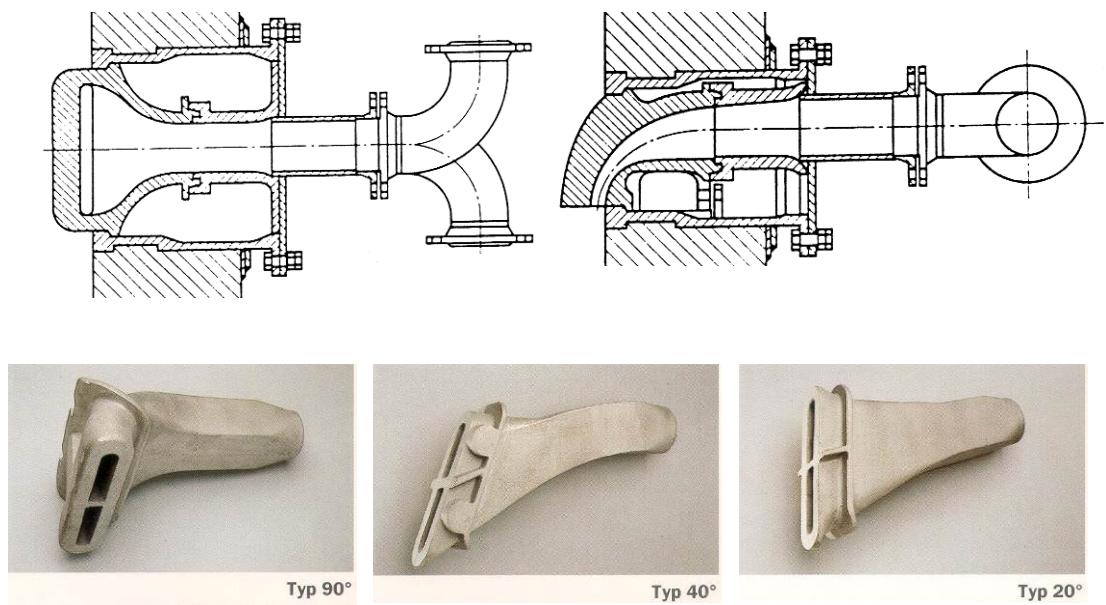


Figure 43: Different nozzle designs mountable to the base frame

The nozzles should never be cast under the new refractory concept (encapsulated lining). At least a separate patch has to be cast around the nozzle to avoid deterioration of the encapsulated lining when the nozzle is exchanged.

For the most critical locations (kiln inlet until orifice), ceramic (only straight) nozzle designs show good performance. Another solution to ensure that well working nozzles are always present at the critical locations is by mounting the nozzle in a box which can be exchanged from the outside (see bottom picture in Figure 44).

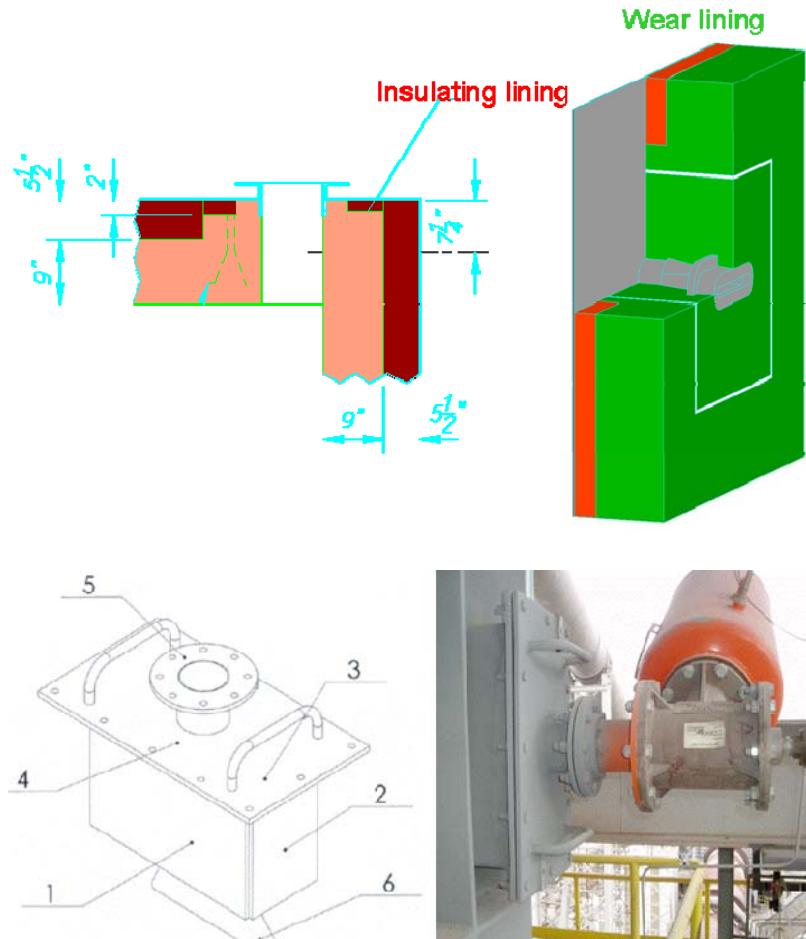


Figure 44: Integration of air blaster in refractory (top), externally exchangeable air blaster in a separate box (bottom)

The direction of the nozzles should always follow the direction of material flow. Normal operating pressures are 5.5-8.5 bars; filtered, dried and lubricated air. Air blasters should have a volume of 100 l in order to efficiently remove build-ups.

Preheater towers heavily loaded with sulfur and/ or chlorine, up to 100 air blasters may need to be installed.

Typical application of air blasters (Figure 45):

- Kiln riser duct and orifice area
- Cyclone cones (up to 10 air blasters may be required in that region), typically a spiral is formed by the air blasters to ensure that cyclone blockages are minimized
- Flat inlets of cyclones
- Meal chutes (nozzles should not be placed near flap gate)

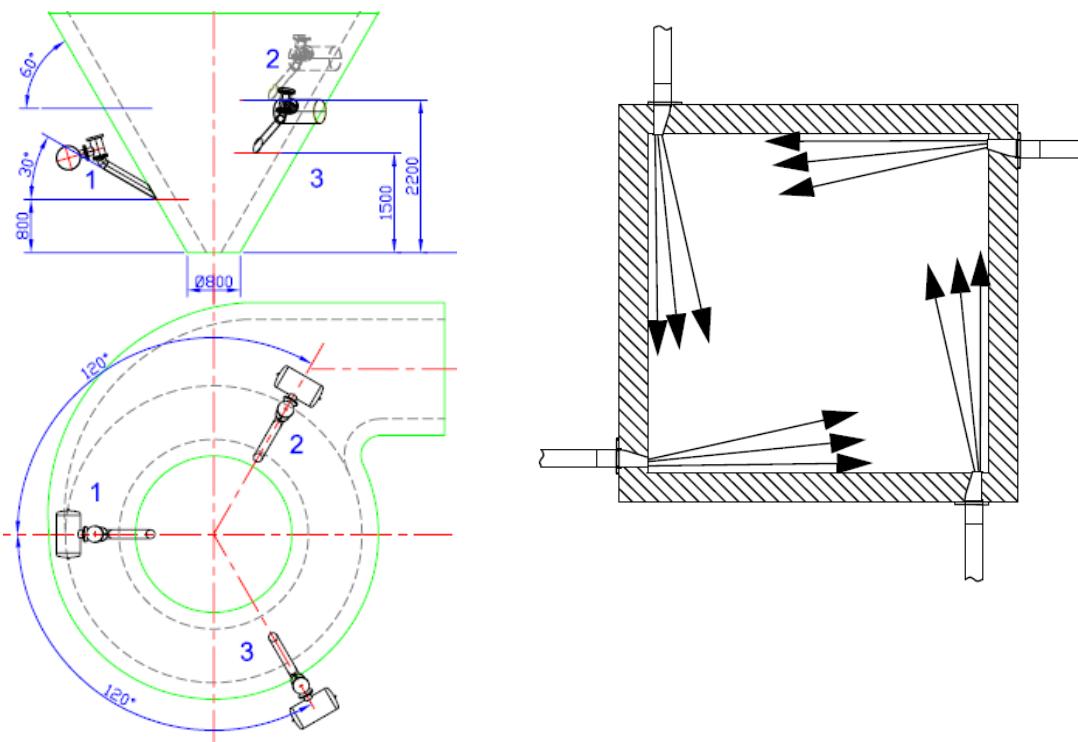


Figure 45: Typical location of air blasters in cyclone cone (left) and kiln riser duct / riser orifice area (right).

Holly Hill plant has installed a new type of air blaster (supplier: Martin Engineering) where one air tank is connected to several nozzles i.e. multiport concept. This can be useful for locations where application area is relatively smaller but requiring multiple air blasters e.g. bypass take off. However the shock will be less powerful due to the long pipe length (avoid rubber pipes for safety reasons).



Figure 46: Multiport air blaster in Holly Hill plant (USA)

Suppliers:

**Big Blaster** from Martin Engineering [www.martin-eng.com](http://www.martin-eng.com)

**Airchoc** from Standard Industries [www.standard-industrie.fr/english/default.asp](http://www.standard-industrie.fr/english/default.asp)

**Vortex Blastair** from Staminair <http://www.staminair.com/>

**Shock Blower** from Agrichema [http://www.agrichema.de/index\\_en.php](http://www.agrichema.de/index_en.php)

#### 10.5.1.9 High-pressure water pump

High-pressure water offers a highly efficient and faster removal of build-ups. However, the refractory lining can get affected by wrong use of this equipment. Since this equipment uses highly pressurized water (300-350 bar), only the certified hoses and connectors should be used. Training of operating personnel is the key for safe operation and higher refractory lifetime.

Key points:

- A T-shaped nozzle should be used to avoid recoil of the single nozzles. Additionally the operator will have more precise cutting of the build-ups, thereby minimizing refractory damages.
- Pressure should be 300-350 bars.
- Moving lances to other platform levels should be avoided for higher lifetime of the lances.
- Monolithic SiC refractory lining should be installed in these zones to minimize the impact of this operation on the refractory lining.
- Good practice is to use this equipment only in the case of very hard build-ups, which cannot be cleaned with the other tools/procedures described earlier.



Figure 47: High-pressure water nozzles (T-shaped nozzle on left)

Supplier: WOMA <http://www.woma.de/home.htm>

#### 10.5.1.10 ATD CARDOX

ATD Cardox system is a powerful system for build-up removal. Carbon dioxide blast effectively removes the build-ups in a safe manner. One big advantage of this system is that opening the big doors is not required. Training of personnel on how to use this system is the key for safe application. In some countries special permits are required for this system.

The system is mostly applied in the preheater tower and cooler area, possible to use also for the rotary kiln (provided sockets are installed).

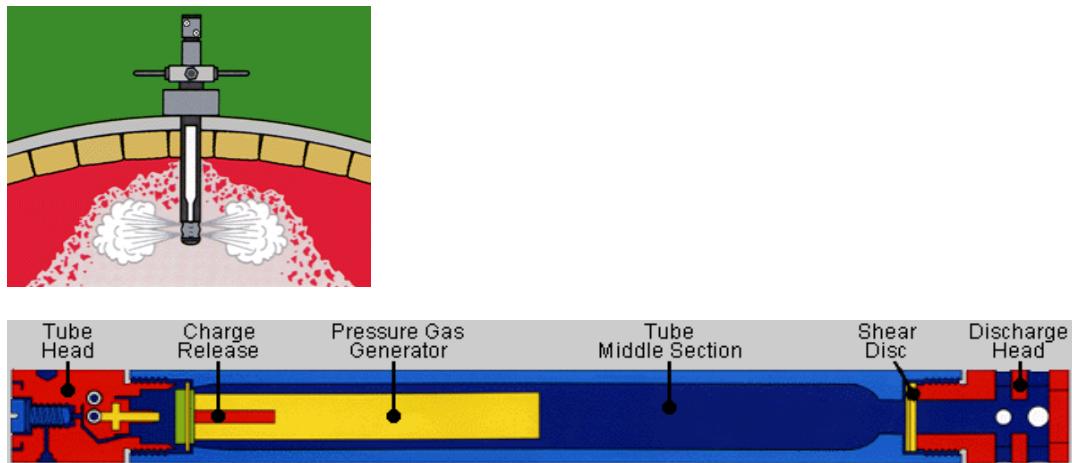


Figure 48: ATD Cardox system

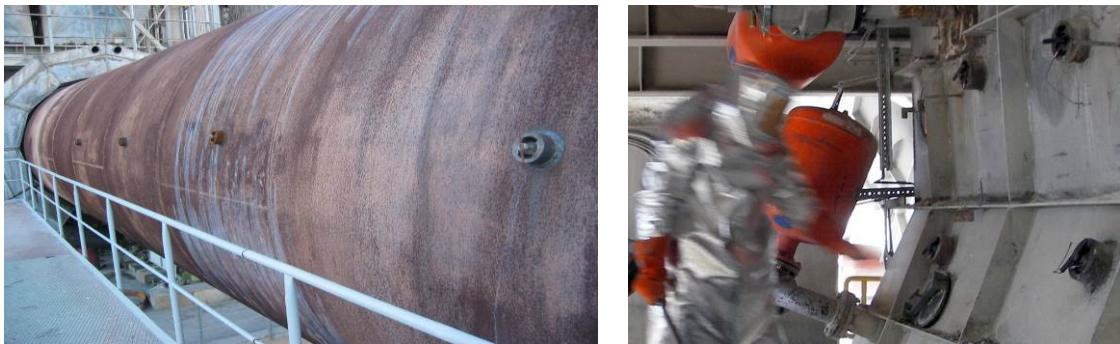


Figure 49: Cardox ports on the kiln shell (left) and around kiln riser orifice (right)  
Supplier: Cardox [www.cardox.co.uk](http://www.cardox.co.uk)

#### 10.5.1.11 Personnel protective equipment

The material used for personal protective equipment must be manufactured from fabrics and other materials which do not promote burning after exposure to and removal from the source of ignition.

As an example, a key characteristic of the protective clothing used for manually clearing blockages on a cyclone is that it should have a limiting oxygen index of 32%, which means a minimum of 32% oxygen is required to maintain combustion. Atmospheric air contains only 21% oxygen and will not support the combustion.

The personnel protective equipment must cover all exposed parts of the body as even 3<sup>rd</sup> degree burns to 12% of the body can be fatal. Always consult your local OH&S personnel in case of any doubt.

Showers and eye washing stations should be made available on all the preheater levels.

#### 10.5.1.12 Cleaning procedure

The following guidelines should always be adapted to the local regulations and to be considered as a minimum requirement. The most critical points are:

##### **Regular shift cleaning**

- Restrict access to preheater tower, clinker cooler and tunnel area during cleaning
- Cleaning crew must always work in pairs, one for cleaning while the other one for communication with CCR
- Wear correct PPE
- Escape path (in upwards direction) has to be clear
- Lock out and release air from air blasters, test to confirm that they are no longer charged with air before opening any inspection door
- Cleaning sequence should be from bottom to top

##### **Cyclone clearing (in addition to the above points)**

- Immediate shut down of the kiln system to minimize the material accumulation in the cyclone
- Warning siren/lights to evacuate people from the PH tower, clinker cooler and clinker tunnel areas
- Cleaning plan should be discussed by the cleaning crew

#### 10.5.1.13 Avoid false air

Any false air infiltration results in local reduction of the temperature. This can facilitate condensation of volatile elements, thereby increasing the chances of build-up formation in the false air entry zone.

#### 10.5.1.14 Coating repellent refractory

The use of coating repellent refractory (high SiC content) provides another option to handle build-ups. This kind of refractory is typically used in critical areas with no or limited access for cleaning operations, to minimize the cleaning requirements. The silica content in the refractory forms up a glassy layer at working temperatures, which in turn inhibits coating formation.

The refractoriness of the high SiC mass is not always sufficient. In case of high secondary firing rates and/or high temperatures at the kiln inlet (1200-1300°C), the glassy layer will melt. For such cases, use combination of ~10% SiC and 10% ZrO<sub>2</sub> refractory (as shown in the following table).

Supplier	For 1200-1300°C area (~10% SiC and 10% ZrO <sub>2</sub> )	For <1200°C area (~30% SiC)
Refratechnik	Refraclay 40 ZAR	Refraclay 40 LLC AR, RefraSiC 50 AR
RHI	Comprit 150 Z, Didoflo 56 ZR	Comprit 123 SiC, Comprit 155 SiC
Calderys	AH 411 SR	Phlocast SiC 30 SR, Monrox SiC 30 SR

Typical locations of high SiC refractory use:

- Material outlet cone of two lowest cyclones
- Bend of the gooseneck of pre-calciner
- Kiln riser orifice area (if temperature is sufficiently low)
- Gas inlets of cyclones (bottom of lowest cyclone and roof of 2<sup>nd</sup> lowest cyclone)

#### 10.5.2 Constructive measures

##### 10.5.2.1 Protection of riser duct

Meal entry to the kiln riser duct should be at lower level so that the volatile elements condense over the meal particle rather than on the refractory walls.

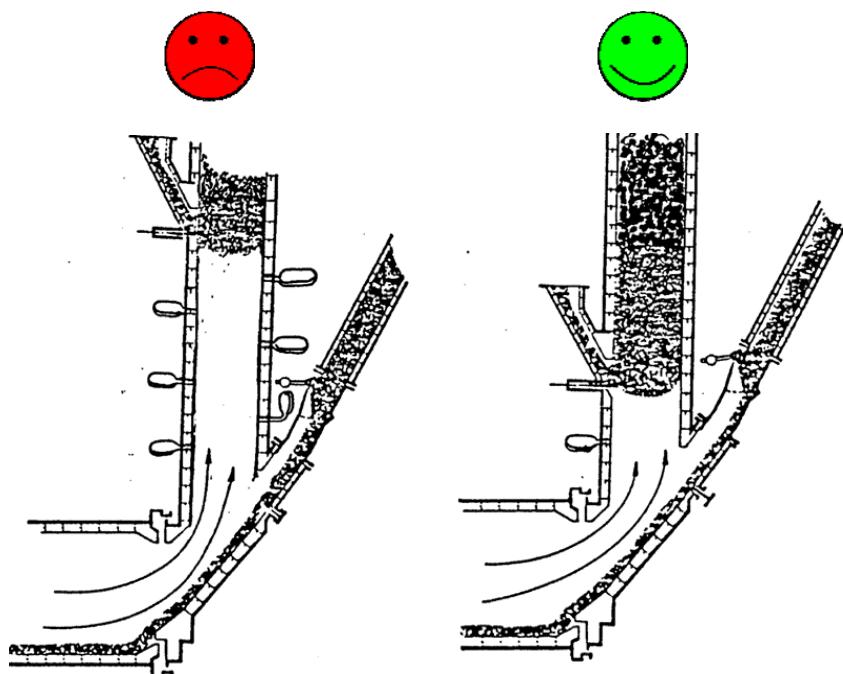


Figure 50: Location of meal splash box

#### 10.5.2.2 Splash box design

A properly operating splash box evenly distributes meal over the entire cross-section of the riser duct, which helps to minimize the build-up formation. To ensure optimal design, 3 elements of a splash box have to be respected:

- No bend in meal duct in the last 2.5 m before the splash box
- Inclination of meal duct before entering the splash box max  $25^\circ$
- Angle between splash plate and axis of meal duct should be  $65^\circ$

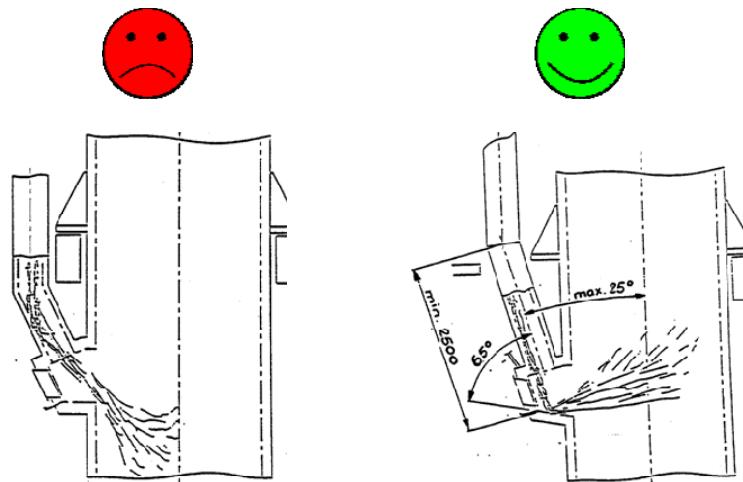


Figure 51: Splash box design

Additionally, the splash box should be located  $>1$  m above the cyclone roof to avoid any material fall-through in the cyclone.

#### 10.5.2.3 Meal flap and duct

Meal flap (or pendulum flap) plays an important role by ensuring hot gases from the lower stage do not bypass the riser duct (i.e. gases go directly into the cyclone cone). The design of the meal flap should allow for full cross-sectional opening. A partially restricted opening could facilitate blockage of the meal pipe.

The inclination of the meal ducts should be  $>55^\circ$ . Inclinations below  $55^\circ$  can promote material deposits and subsequently lead to cyclone blockages.

#### 10.5.2.4 Cyclone outlet and meal pipe bends

In case of older preheater towers with smaller cyclone, the meal pipe diameter could be too small. Additionally, meal pipe cross-section reduces around bends, potentially favouring blockages of the pipes e.g. material coatings falling into the meal duct.

Figure 2 shows a modification done at Siggenthal plant wherein the outlet of the bottom stage cyclone was enlarged. Also the bend in the meal pipe (immediately after the cyclone outlet) was removed by redesigning the meal pipe.

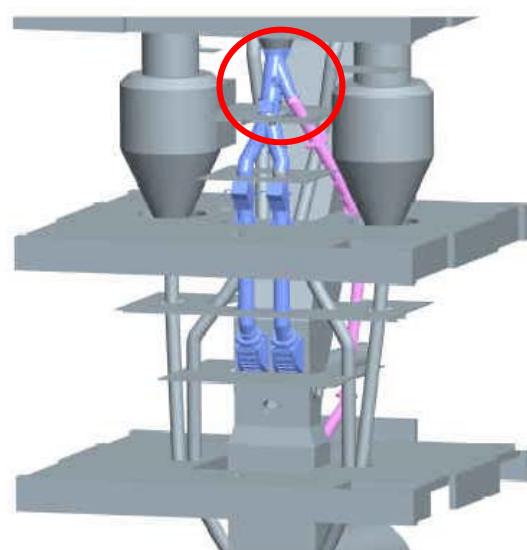


Figure 52: Enlarged outlet of lowest stage cyclone in Siggenthal plant (RED line indicates old design – not to scale)

#### 10.5.2.5 Meal curtain

A meal curtain is an arrangement where about 10-25% of the material from 2<sup>nd</sup> or 3<sup>rd</sup> lowest cyclone stage is introduced into the kiln inlet chamber. The colder material (from 2<sup>nd</sup> or 3<sup>rd</sup> stage) promotes condensation of the volatile elements which then latch onto the meal particles instead of on the refractory walls.

Good experiences have been made with meal curtain retrofits. Figure 53 depicts a meal curtain installation by Polysius.



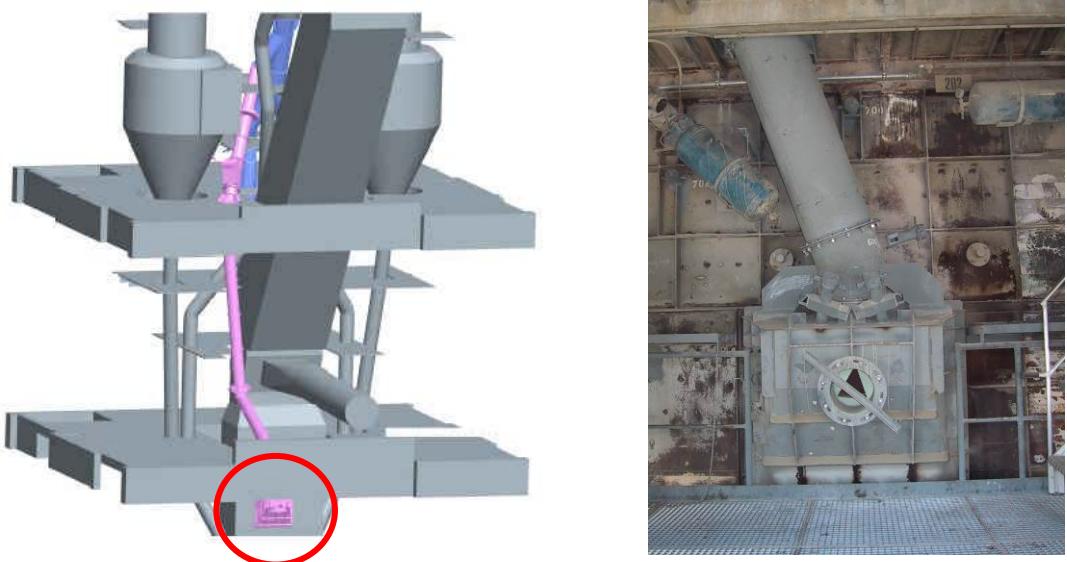


Figure 53: Meal curtain (source: Polysius)

#### 10.5.3 Kiln inlet O<sub>2</sub> control

Laboratory tests of the primary volatility  $\epsilon_1$  (volatility of sulfur when exposed the first time to high temperatures) show that already at a temperature level of 1000°C, the sulfur volatility goes up close to 1 (100% volatility), if there is no oxygen in the kiln atmosphere. This is the case if the fuel produces a local reducing condition in the kiln charge material (e.g. when burning whole tires at the kiln inlet).

From these tests it can be derived that the main influence of the oxygen on increase of sulfur volatility is produced between 0 to 2% O<sub>2</sub>. Beyond 2% O<sub>2</sub> the influence is negligible.

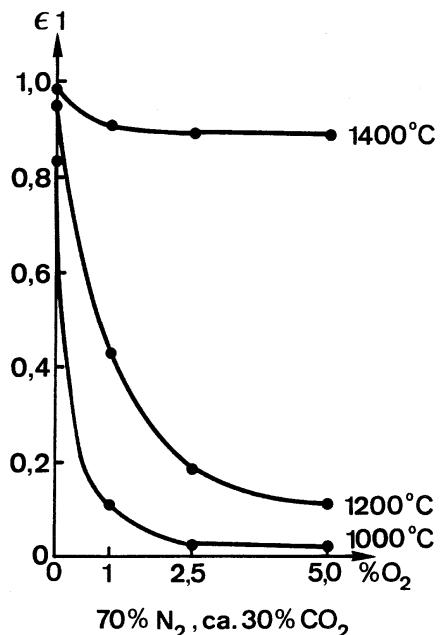


Figure 54: Influence of oxygen (and temperature) on sulfur volatility

For this reason a reliable O<sub>2</sub> measurement at the kiln inlet is essential. A well-functioning tertiary air damper (TAD) is equally important to control the O<sub>2</sub> at kiln inlet. Best results have been achieved with forced air cooled guillotine type dampers in horizontal ducts and ELKEM ([www.elkem.com](http://www.elkem.com)) ceramic precast dampers in vertical ducts.

Targets of kiln inlet oxygen depend on different factors such as the sulfur volatility, the energy split between main burner and pre-calculator, and the ability to move the tertiary air damper. With AFR and/or Petcoke, the following targets should be respected.

Kiln system	Kiln inlet oxygen vol%, dry
PC – Pre-calculator (ILC)	2.5-4
PC – Pre-calculator (SLC)	2-3
SP – Suspension preheater	2-3
DG – Grate preheater (Lepol)	2-3
WL – Long, wet	2-2.5

The increased oxygen content compared to coal will result in a production loss if the gas flow (e.g. ID fan, system fan) is the limiting factor.

#### 10.5.4 Burning zone temperature control

Besides oxygen, the peak temperature the material reaches is another influence factor on sulfur volatility. For this reason the control of these two parameters needs to be handled more strictly. The operator needs to be aware of these factors as well as the instrumentation (kiln inlet probe, BZT) and the actuators (tertiary air damper, coal feeders). A good maintenance regime is required to ensure good availability of the equipment / instrumentation.

The clinker is typically dustier when petcoke is used as a fuel. The increased SO<sub>3</sub> content has multiple effects. It lowers the surface tension of the liquid phase and, additionally, it acts as a flux lowering the theoretical burning zone temperature. The lower temperature and the lower content of liquid phase all together with the lower surface tension lead to more difficult granulation, which results in finer (dustier) clinker.

With the dustier kiln atmosphere, it becomes difficult to interpret the signals used for detection of the burning zone state. For this reason it is not recommended to use just the one indicator for the burning zone observation, rather several indicators should be used to draw the correct state of the BZ. Below is a list of possible measurements to estimate the BZ state.

##### 10.5.4.1 Pyrometer

1-wave length type pyrometers measure only the intensity. On the other hand, 2-wave length type pyrometers measure the frequency (colour) and are, for this reason, less susceptible to dust.

Typically the pyrometer measures the temperature near the drop-off point where the clinker leaves the kiln. A kiln camera is the better alternative to a pyrometer since the measurement locations can be changed easily.

#### 10.5.4.1.1 Kiln camera

With the use of multiple AFRs, the quality of the traditional process parameters (kiln torque and NOx) degrades so additional signals are required. The following kiln cameras are recommended by HTEC:

- Pyroviper from Gesotec
- PiT Multisensor from Powitec
- Thermascope SLK from Thermoteknix
- Pyroscan 28 from HGH
- VTA 200 from Durag
- Tempera from Technologia Integrale

These cameras produce a video signal of the burning zone and in the image the temperature measurement zones can be defined.

Typical locations for measurement spots:

1. Clinker before leaving the kiln
2. Clinker further back in the kiln
3. Side or bottom of burner refractory (secondary air temp)

#### 10.5.4.2 Secondary air temperature (to facilitate interpretation of BZT)

This measurement reflects only the tendency and typically not absolutely correct. SAT is located on top or either side of the kiln hood. In pre-calciner kilns with extraction of the tertiary air from kiln hood, this measurement can be done some meters inside the tertiary air duct to receive a more accurate value. With an acoustic thermometer ([www.enertechnix.com](http://www.enertechnix.com)), the temperature could be measured more accurately.

#### 10.5.5 Kiln speed control

With the different granulometry of the clinker the feed to speed relation may need adjustment. Typically the kiln filling degree needs to be lowered with finer clinker. Finer clinker will need less residence time in the burning zone. Additionally the kiln speed needs to be increased due to the lower transport efficiency finer clinker has in comparison to coarser clinker.

Experience will show if a speed change (if possible) will improve general kiln stability and free lime distribution.

#### 10.5.6 Cooler control

##### 10.5.6.1 Planetary cooler

With planetary cooler there are no operational measures to minimize the dust entrainment in the kiln caused by the finer clinker.

#### 10.5.6.2 Grate cooler

In order to minimize the dust entrainment in the kiln, typically the air in the fixed inlet is reduced. The aeration in the first chambers of the moving grate is increased to maintain total specific aeration constant. Snowman formation can be a result of this change which needs to be carefully observed when changes are done to the aeration pattern.

#### 10.5.7 Pre-calciner control

Pre-calciner operation is typically not affected by the use of petcoke if the burnout of the fuel is given. Typically a new target temperature for the pre-calciner fuel controller needs to be found. Typically the exit temperature needs to be increased to achieve the same decarbonization rate due to the higher O<sub>2</sub> targets.

#### 10.5.8 Kiln feed uniformity

Consistent kiln feed composition is the key to higher petcoke utilization. Kiln feed variations increase the process instability and result in further volatilization of sulfur. All possible measures to improve the kiln feed uniformity should be explored. The Holcim uniformity targets for kiln feed (and clinker) are:

Parameter	Short-term (1-month average of daily standard deviation on hourly basis)	Long-term (1-month standard deviation of daily averages)
LSF	< 1.2	< 1.0
SR	< 0.04	< 0.03
AR	< 0.04	< 0.03

Additional guide values for clinker uniformity are:

Parameter	Daily (based on hourly samples)
CaO <sub>f</sub> range (min-max %)	≤ 0.8
SO <sub>3</sub> C.o.V.	≤ 10
K <sub>2</sub> O C.o.V.	≤ 10

For petcoke use, the short-term kiln feed and clinker-specific uniformity are the most critical. Kiln feed dosing fluctuation should also be minimized, with short term fluctuations (10 seconds) < 1%.

#### 10.5.9 Fuel uniformity

Along with kiln feed uniformity, the uniformity of fuels is also important for higher petcoke utilization on sustainable basis. The coal and/or petcoke uniformity guidelines are:

Type of fluctuation	Guide value
Short-term feed	< 1%
Short-term C.o.V.	< 1%
Pressure in transport line (at burner)	< 10%

### 10.5.10 Burnability

Improved burnability of the kiln feed will also help minimize negative effects of petcoke. The effect is mainly due to the more moderate burning regime, thereby decreasing the volatilization of sulfur from the clinker bed. Holcim Burnability Test (HBT), as carried out at HTEC/CM-QPC, provides a definitive evaluation of the burnability of the kiln feed.

Another way to determine burnability behavior is through the calculation of combinability temperature<sup>1</sup> (CT).

$$CT = 436 + 21 \cdot AIR_{90\mu KF} + 10 \cdot LSF_{cli} + 3 \cdot R_{150\mu KF} + 32 \cdot AR_{cli} - 250 \cdot F_{cli} - 20 \cdot SO_3_{cli}$$

where,	CT	= Combinability temperature, °C
	AIR <sub>90μKF</sub>	= Acid insoluble residue on 90μ of kiln feed, %
	LSF <sub>cli</sub>	= LSF of clinker, -
	R <sub>150μKF</sub>	= Residue on 150μ of kiln feed, %
	AR <sub>cli</sub>	= Alumina ratio of clinker, -
	F <sub>cli</sub>	= Fluorine content of clinker, %
	SO <sub>3cli</sub>	= SO <sub>3</sub> content of clinker, %

Although CT is not as accurate as HBT, it provides reasonable accuracy and is easier to calculate as all the required parameters can be determined in a plant laboratory. A user-friendly CT spreadsheet tool is available on iShare\Manufacturing and Processing\Petcoke.

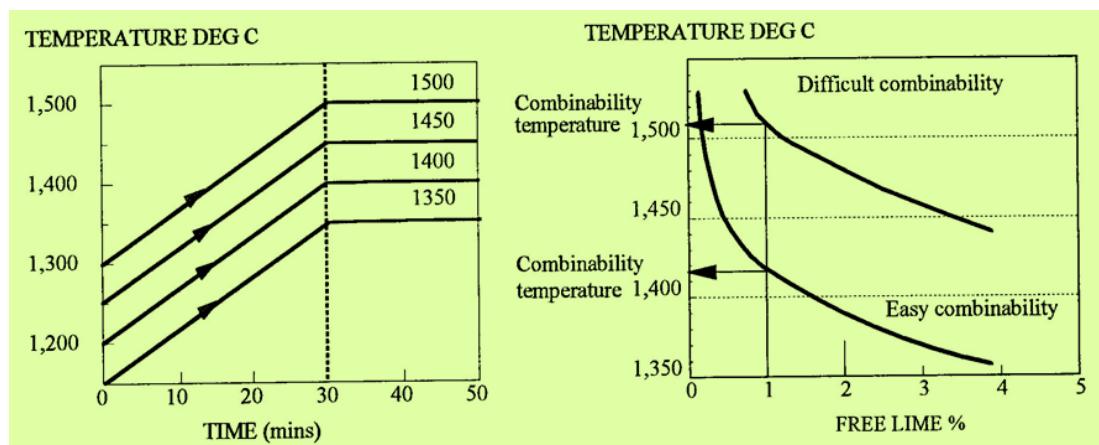


Figure 55: Combinability test heating regime (left) and typical combinability curves (right)

The most typical way to affect burnability is by adjusting the moduli of the raw meal. Ensuring LS (lime saturation) is at an optimal value for the kiln is of utmost importance. As hard burning increases sulfur volatilization, an appropriate free lime target should be kept and controlled. A too low free lime target will result in enhancement of the sulfur cycle and increased build-ups. Hard burning increases

<sup>1</sup> Combinability temperature concept was developed by G.K. Moir by analysing burnabilities of kiln feeds of 15 cement plants in the laboratory, using a horizontal programmable tube furnace ( reference: Moir, G.K. 1997, Influence of raw mix heterogeneity on ease of combination and clinker strength potential. 10th International Congress on Cement Chemistry, Gothenborg, Sweden)

the sulfur volatilization due to both evaporation and the breakdown of sulfates. Silica ratio (SR) and alumina ratio (AR) can also be adjusted to improve the burnability. A better burnability can also be achieved by finer grinding of the raw meal.

Another way to improve burnability is by mineralization i.e. by adding fluoride to the raw mix. As a prerequisite, mineralization requires very good control of the process. It can offer an improvement once all the other optimizations have been made. Guayaquil plant (formerly Cerro Blanco) in Ecuador is an example of improved burnability allowing 100% petcoke utilization even with very low alkalis ( $\text{Alk}/\text{SO}_3$  ratio down to 0.2!). Guayaquil plant uses both a fine raw meal ( $R_{90\mu\text{m}}$  14%,  $R_{200\mu\text{m}}$  0.6%) and fluoride mineralization to improve the burnability. While mineralization normally leads to higher alite content in clinker (70-75%), at Guayaquil the mineralization is devoted to allowing higher sulfur level in the clinker and maximizing the petcoke use.

#### 10.5.11 Optimizing clinker granulometry

A higher utilization of petcoke usually results in increasingly dusty clinker along with a dustier kiln atmosphere. This is generally believed to be due to the reduction of the liquid phase's surface tension and thereby the ability to stick and hold fine particles. It has also been suggested that the breakdown of the temperature-sensitive sulfur-bearing minerals in the clinker bed (alkali-sulfates, Ca-langbeinite, anhydrite) may create further dust - when a grain breaks down, a pore space results, thereby making the clinker more susceptible to fracture and dust generation.

In addition to changing the raw meal moduli to improve burnability as described in the previous section, reducing the SR will increase the volume of liquid phase and result in a larger liquid surface area where dust can stick. Increasing the AR can help by making the liquid phase more viscous and thus producing larger clinker nodules which are less susceptible to sulfur loss. Caution must be exercised with SR and/or AR adjustments as a change may also bring thicker coating and higher likelihood of sinter ring formation.

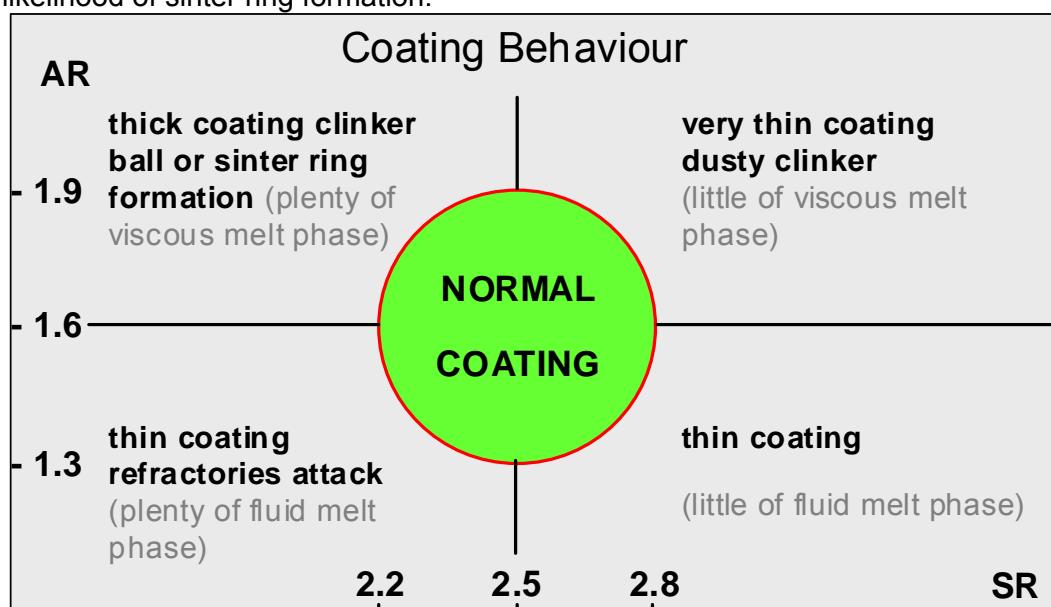


Figure 56: Coating behaviour as a function of silica ratio (SR) and alumina ratio (AR) in clinker

#### 10.5.12 Raw materials/mix optimization

The raw materials/mix used by the plant can also be changed to avoid some of the negative effects of petcoke, most obviously being the sulfur input. As the total sulfur input from fuel and raw materials is important, reducing input from the raw materials can allow higher-S fuel (or increased amounts of high-S fuel). Another option to compensate the increased sulfur is by using the alkali-rich raw materials, thereby balancing the Alk/SO<sub>3</sub> ratio and removing the sulfur from the kiln in the form of clinker alkali sulfates.

As an example, Chekka plant in Lebanon changed from using 1.8% SO<sub>3</sub> clay to a low grade limestone and thereby reduced the sulfur input from raw materials from 0.47% to 0.01% to increase the petcoke utilization.

### 10.6 Challenges - Refractory and corrosion

#### 10.6.1 Refractory

The use of petcoke as a fuel for the cement kiln can have effects on the refractory due to:

- Higher sulfur input
- Flame changes due to higher fuel variation
- Areas of reducing conditions due to slower petcoke burn-out

The higher sulfur input can lead to excess sulfur content in the kiln. If this is the case, the sulfur will attack any CaO-phase (and Ca-Silica phases) present in the refractory, forming Anhydrite or S-spurrite. Thus dolomite bricks, which may be used in the sinter zone, become especially susceptible to premature failure due to their high CaO content.

In Magnesia and Magnesia-spinel bricks (sinter and transition zones), the sulfur attack is limited to the silicate bond and thus less problematic in the mostly ceramic-bonded magnesia. For high alumina refractory used in the kiln and hot static areas, sulfur attack is not a major problem – in fact the tendency to reduce alkali volatilization could actually improve their lifetime due to reduced alkali-attack of the alumina.

Fireclay bricks are more susceptible to sulfur attack due to their higher silica content. However as they are normally installed in colder areas of the kiln beyond the boundary of the kiln sulfur cycle, sulfur attack due to petcoke use is generally not a problem.

Flame changes due to inconsistent fuel properties can be exaggerated when using petcoke without appropriate process control. These changes will cause unstable coating formation in the upper and lower transition zones of the kiln resulting in brick hot face spalling and thermal shock to the lining. These effects can significantly reduce brick lifetime.

Again if the process is not well controlled and reducing conditions occur (local or more widespread), the lifetime of especially magnesia bricks will be reduced due to the volume changes associated with volume changing redox action on iron impurities within the magnesia grains leading to cracking.

#### 10.6.1.1 Use different basic kiln bricks

Often the use of petcoke can lead to less stable burning conditions as compared to coal-firing. Less stable burning results in unstable coating formation in the upper and lower transition zones which in turn causes frequent thermal stress on the basic bricks in those zones (whenever the coating falls off the brick, the brick is suddenly exposed to higher temperatures). These thermal stresses cause degeneration of the bricks due to cracking of the brick grains from the stress.

If, with the use of petcoke, brick lifetime in the upper and lower transition zones is reduced significantly, it should be considered to use more flexible and more coating stable materials. The normal additive to basic ( $MgO$ ) bricks to improve their flexibility (i.e. thermal stress resistance) and improve coatability is spinel, making "Magnesia-spinel" bricks.

An improvement on traditional magnesia-spinel bricks is the developments of Hercynite and Galaxite bricks which offer even better flexibility and coating behavior for particularly problematic situations.

#### Rotary kiln

- Check if zones need to be adjusted (longer BZT? longer upper transition zone?)
- If the coating is no longer stable in the upper transition zone coating repellent bricks should be used
- Use of alkali resistant lining in the kiln

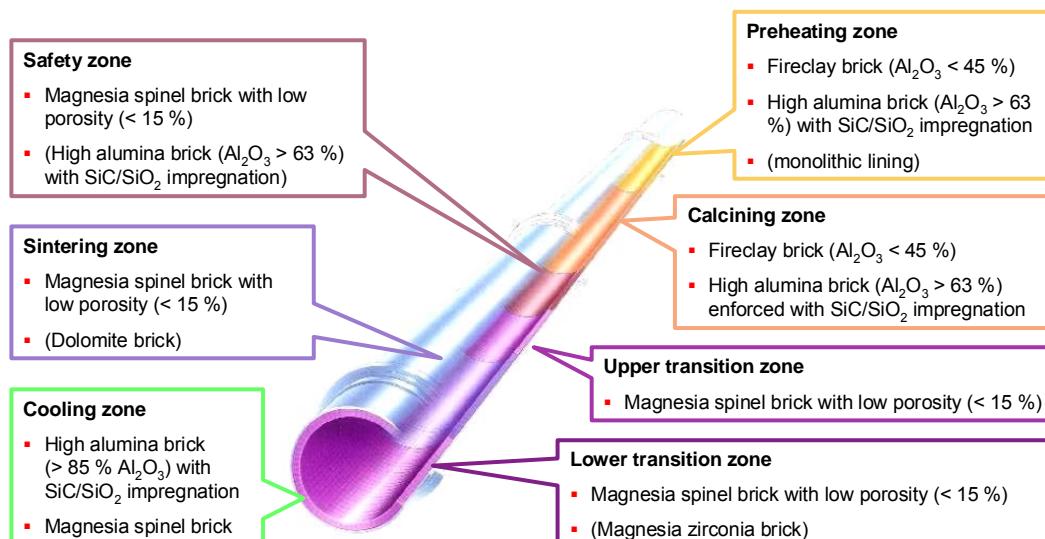


Figure 57: Recommended bricking regime for rotary kiln

### Increased abrasion

The higher dust content will typically increase the abrasion in the critical zones, for this reason check more frequently than before the critical areas:

- Cooler bull nose (correct installation and cooling)
- Nose ring
- Tertiary air damper
- Elbow of tertiary air pipe in SLC kilns

Also, here the installation of refractories high in SiC can improve the situation.

## 10.6.2 Corrosion

Due to the higher input of sulphur by petcoke compared to regular coal, there is the risk of increased acid and high temperature corrosion. There is no influence on acid corrosion phenomena in main filters or stacks as long as all the sulphur from fuel is scrubbed by raw meal and is leaving the system with the clinker as it is the case in dry preheater/pre-calciner kilns without bypass.

### 10.6.2.1 Theoretical Background

There are basically three different corrosion mechanisms that can occur in a cement kiln system. In particular concerned are inner surfaces (behind refractories), steel anchors and the clean gas plenum of a filter.

- **Oxidation (rusting)**

Oxidation at temperatures around the water dew point or below may affect exhaust filter, steel construction, preheater tower, kiln shell (during shutdown) and gas ducts

- **Acid corrosion**

Corrosion at temperatures around the acid dew point or below may affect preheater tower, kiln hood, kiln shell (e.g. behind rings), gas ducts and exhaust filter (hot gas filters)

- **High temperature corrosion**

Reaction of gaseous sulfur and chlorine with Fe, Ni and Cr may affect preheater tower (hot zones), kiln hood, kiln shell, immersion duct / dip tube

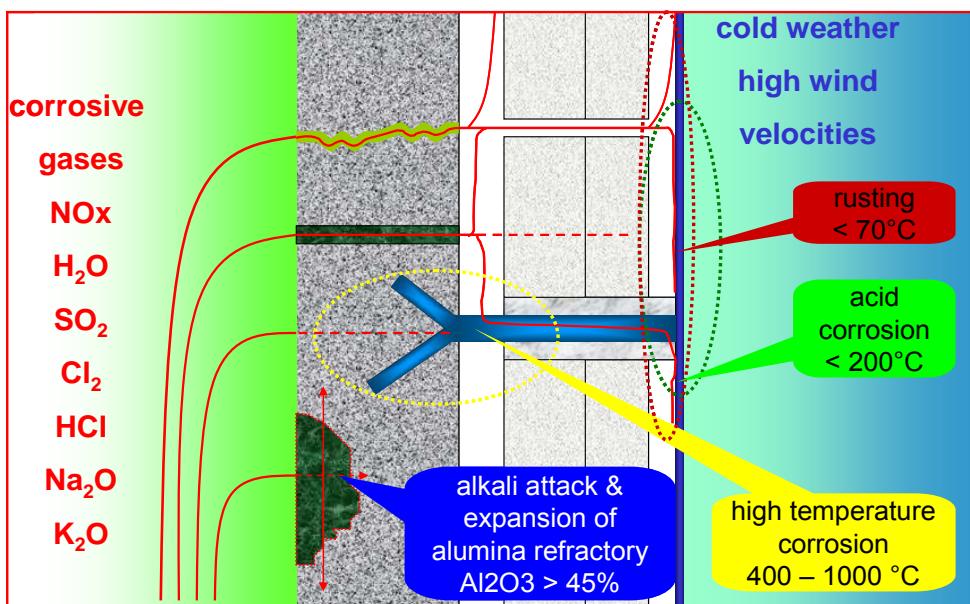


Figure 58: Corrosion mechanism in a 3-layer refractory lining

The acid corrosion is an electrochemical process that is happening at temperatures below the acid dew point, which directly depends on the SO<sub>3</sub> (1-3% of SO<sub>2</sub>) content of the gas. The acid dew point is higher than the water dew point since H<sub>2</sub>SO<sub>4</sub> condenses already at higher temperatures than steam.

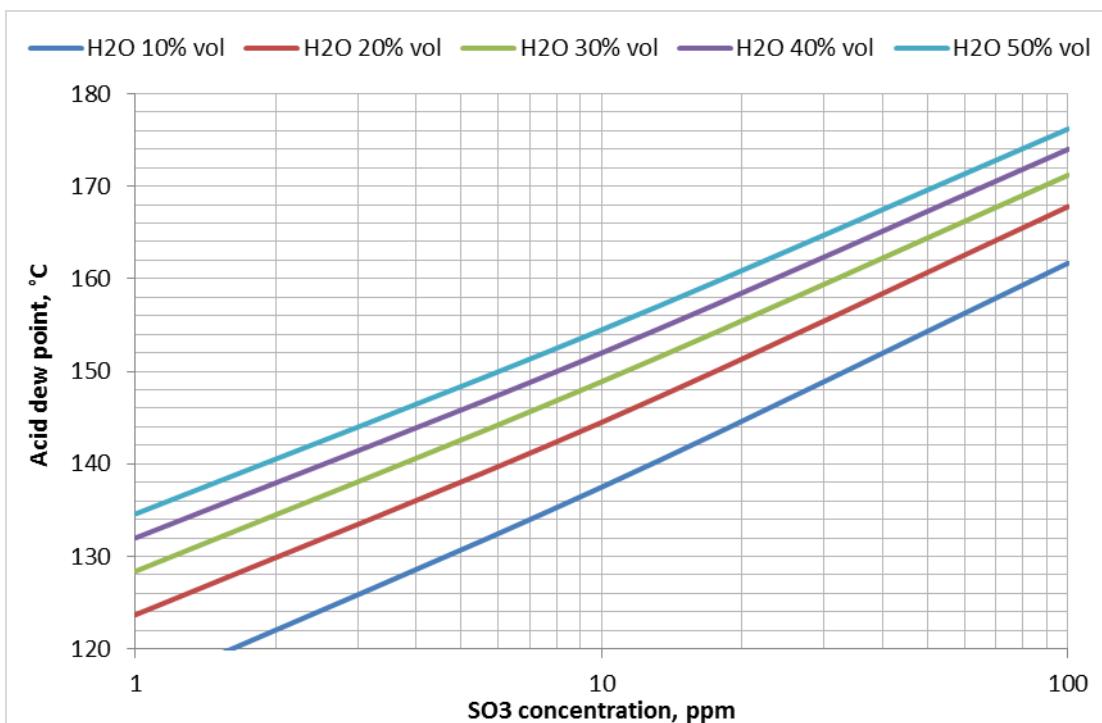


Figure 59: Acid dew point at different SO<sub>3</sub> / H<sub>2</sub>O concentrations (P<sub>s</sub> 1'000 mbar)

The high temperature corrosion can be described by a direct reaction of sulfur and chlorine gases or melts of alkali salts with iron, nickel or chrome and takes place at temperatures above 400°C.

#### **10.6.2.2 Measures to minimize corrosion impact**

The appropriate measure depends on the type of corrosion.

- Minimize corrosive gases input (Raw material and fuels)
- Temperature management to prevent high temperature corrosion: Inner insulation against high temperatures at metal surface
- Temperature management against acid corrosion and rusting: keep surface temperatures high, i.e. minimum 20°C above acid dew point (Holcim refractory concept / High temperature filter / Outside insulation of filters / Prevention of cold bridges / Prevention of frequent start-stop operation)
- Protective coating for kiln shell (Corr-Paint, KilnGard) and clean gas part of the process filter (FlueGrad, Epoxy resin)
- Avoid excessive moisture (water injection mill, conditioning tower, raw material storage)
- Selective use of high alloy steel qualities (Chlorine pitting!) / Use alternative materials (e.g. ceramic anchors)
- Enhance sulfur scrubbing: Measures against sulphur volatility / raw mill operation time / hydrated lime injection etc.
- Periodical steel shell measurements (thickness, appearance)

The Holcim refractory concept is based on three pillars to mitigate the impacts on corrosion and refractory attacks:

Higher wall temperatures

- no acid condensation on steel

Gas-tight capsulated lining

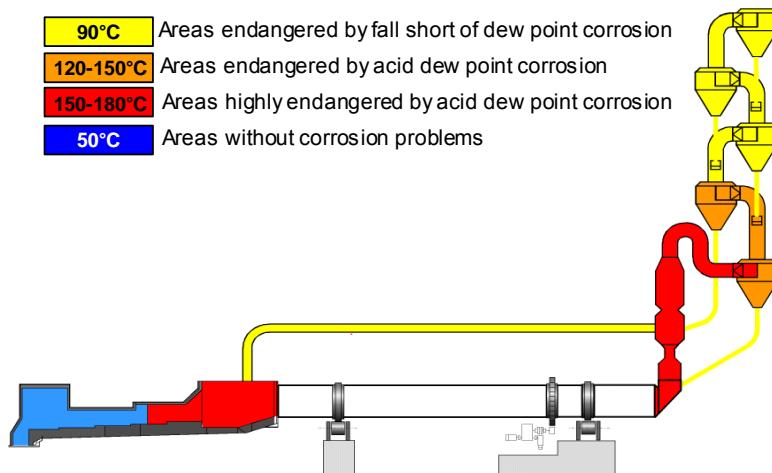
- anchors and support flanges are protected against the corrosive gases

Use of alkali resistant refractory

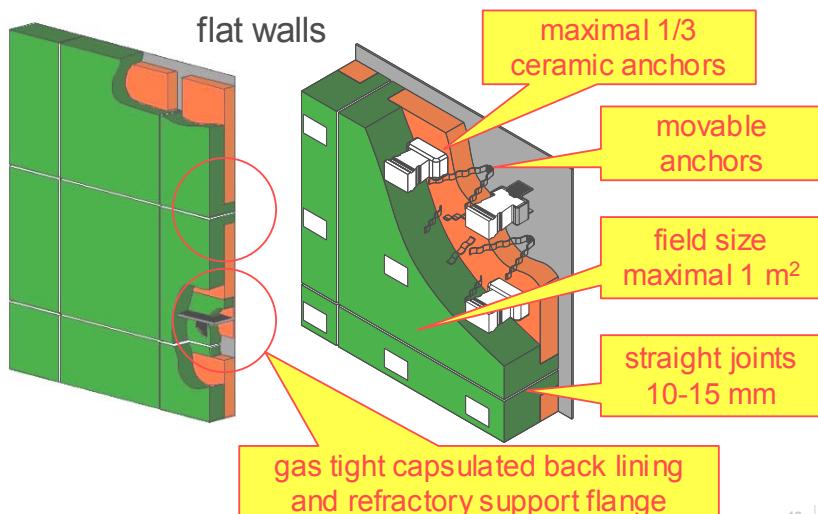
- Avoid alkali spalling and refractory expansion

### Solution (1): increased wall temperatures

<b>90°C</b>	Areas endangered by fall short of dew point corrosion
<b>120-150°C</b>	Areas endangered by acid dew point corrosion
<b>150-180°C</b>	Areas highly endangered by acid dew point corrosion
<b>50°C</b>	Areas without corrosion problems



### Solution (2): Gas tight capsulated monolithic lining



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Figure 60: Holcim refractory concept (for more details, see report TPT 05/21369/E)

This concept should be considered for all refractory repairs if AFR and/or petcoke are used.

## 10.7 Challenges - Clinker and cement quality

The use of petcoke can have a significant effect on clinker quality, and therefore on cement and concrete quality.

### 10.7.1 Raw mix

When switching from coal to petcoke, normally the raw mix must be changed to account for the low amount of ash in petcoke. As the raw mix composition is tailored to produce clinker of a certain composition, the lack of ash contribution when using petcoke has to be taken into account.

It must also be noted that excess sulfur that is not balanced by alkalis will bind Ca in clinker to form Ca-langbeinite and anhydrite. This results in reduced availability of Ca for the formation of alite and effectively reduces the clinker lime saturation. This effect can be compensated by increasing the lime saturation of the raw mix. The amount of increase can be calculated if the content of Ca-S phases in clinker is determined by microscopy or X-ray diffraction (Rietveld).

#### 10.7.2 Clinker quality

##### 10.7.2.1 Alite ( $C_3S$ )

Apart from the potential negative impact on alite content in clinker mentioned above, use of petcoke also has an effect on the grain size of alite. The slower burn out and longer flame normally associated with petcoke results in a longer burning zone and thus 'hard burnt' clinker. Such clinker contains larger alite grains (due to longer times at high temperature) which require higher grinding efforts and have a reduced reactivity.

##### 10.7.2.2 Aluminate ( $C_3A$ )

In clinker with a significant excess of alkalis over sulfur, alkalis incorporate into  $C_3A$  and stabilize the orthorhombic form (instead of the cubic form), which may cause a disturbed setting behavior of cement. With the addition of sulfur to clinkers with high amount of unbalanced alkalis (e.g. by petcoke), the alkalis will form alkali sulfates rather than entering the  $C_3A$  structure, providing more 'normal' setting behavior.

##### 10.7.2.3 Cement setting time (gypsum dosing optimization)

The use of petcoke will normally extend setting times due to the increased clinker alkali sulfate content (due to lowering the Alk/ $SO_3$ ), although early strengths are improved. If there is a strong sulfur excess over alkalis, anhydrite may form in the clinker further retarding setting times.

Therefore, when switching from other fuels to petcoke, a gypsum optimization has to be carried out on cement. A procedure to perform a gypsum optimization is presented in Annex 6.

The higher clinker sulfate content is expected to reduce the amount of gypsum needed for cement setting control for the reasons mentioned above. Furthermore, the  $SO_3$  content of cement is limited by cement standards such that in some cases increased  $SO_3$  content in the clinker requires reduced gypsum content in cement to meet the standard.

#### 10.7.3 Color

The use of petcoke can have an effect on the final cement and concrete color. There are two main effects which may cause a color change:

- Local reducing conditions: can result in a brown coloration in affected clinker nodules and result in a browner color of cement and concrete.
- Reduced coal-ash input: The effect of the coal ash in the clinker and thereby cement will be reduced or eliminated with the use of petcoke, this can thereby lead to a changing of the shade of the resulting cement and concrete.

## **10.8 Challenges - Stack emissions**

### **10.8.1 NO<sub>x</sub> emissions**

There are two different NO<sub>x</sub> formation mechanisms in the cement burning process. Thermal NO<sub>x</sub> is formed at the main flame at elevated temperatures (>1500°C) while fuel NO<sub>x</sub> is mainly formed in the secondary firing or calciner at 800-1200°C.

Sources of NO<sub>x</sub> are the oxygen in the combustion and false air as well as the nitrogen in air (thermal NO<sub>x</sub>) or the nitrogen bound in the fuel (fuel NO<sub>x</sub>).

NO<sub>x</sub> can be partly reduced in the system. Hydrocarbon radicals arising from the calciner/secondary fuel are reacting with NO to form nitrogen. Certain conditions like hot spot (~1050-1200°C) and reducing conditions (lack of oxygen) in a restricted area of the calciner favours this reduction mechanism (low NO<sub>x</sub> calciner principle). The higher the fuels volatile content the better the reduction effect.

The following effects enhance NO<sub>x</sub> formation when changing from coal to petcoke:

- In case the **nitrogen content** of petcoke is more than coal. The more nitrogen input, the more NO<sub>x</sub> is formed.
- Petcoke is **less reactive**. The ignition happens with a higher delay (longer distance burner and flame front); there is more time for the mixing of fuel and air. The better the oxygen entrainment into the flame/combustion zone, the more NO<sub>x</sub> is formed.
- With an increased draft and/or primary air rates, that are required to lower the sulphur volatility, there is a higher **oxygen level** available in the kiln burning zone. The higher the amount of oxygen in the combustion area, the more NO<sub>x</sub> is formed (up to a certain level of O<sub>2</sub>)
- Higher main **burner momentum** due to the more difficult to burn fuel. Total momentum affects the overall entrainment of air into the flame jet. In general, higher momentum results in enhanced mixing, higher flame temperature and therefore higher thermal NO<sub>x</sub>.

The following effects hamper the NO<sub>x</sub> reduction when changing from coal to petcoke:

- The **volatile matter content** in petcoke is less than coal, hence fewer hydrocarbons are formed. Local reducing conditions are not created to the same extent, thus less NO<sub>x</sub> is destroyed.

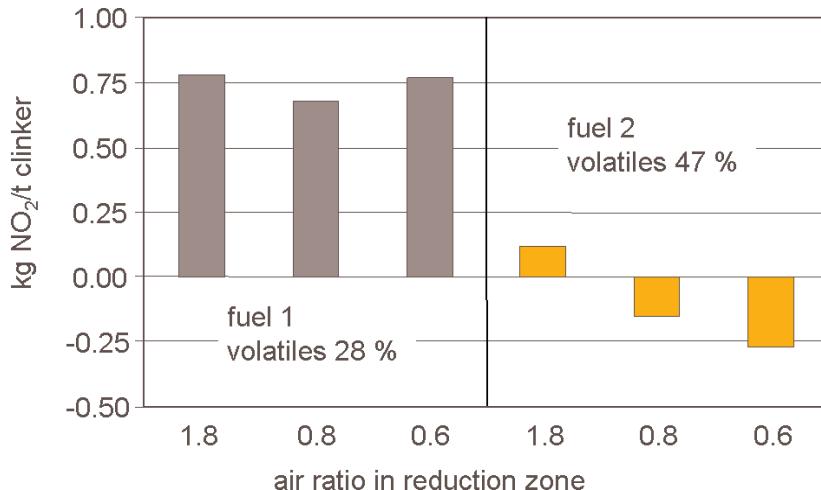


Figure 61: Calciner NO<sub>x</sub> - Success of NO<sub>x</sub> reduction in calciner as a function of volatiles and air ratio (source: ECRA)

The following effects hamper the NO<sub>x</sub> formation when changing from coal to petcoke:

- Increased sulphur input is lowering the burning zone temperature (dust)

#### 10.8.1.1 Experiences

- Petcoke in Guayaquil (Holcim Ecuador, PC kiln)

NO<sub>x</sub> emissions increase with petcoke by about 400-500 mg/Nm<sup>3</sup>

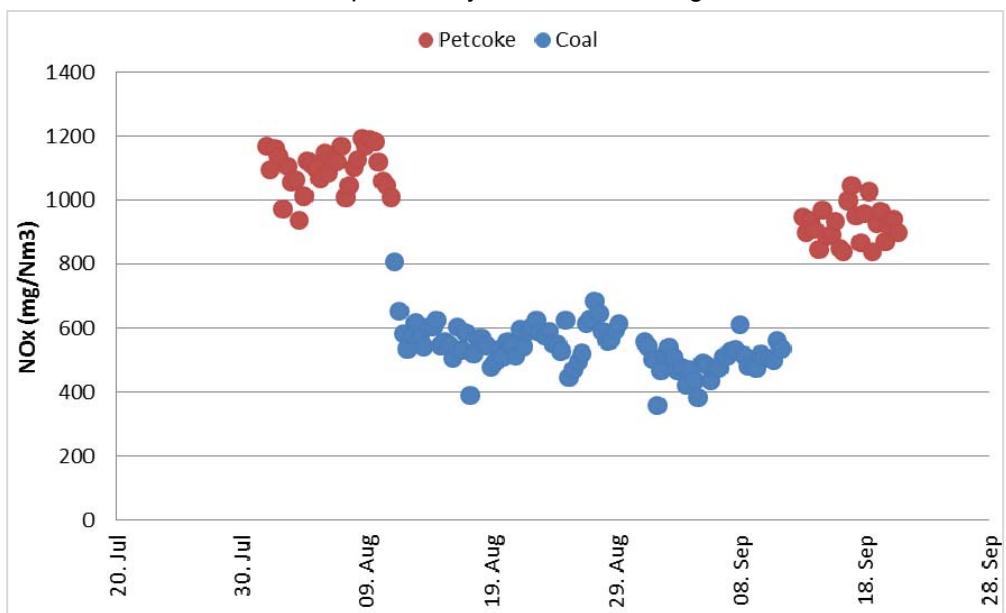


Figure 62: Petcoke and coal influence on NO<sub>x</sub> emissions in Guayaquil (2009 data for kiln 2)

- Petcoke increase in Dundee (Holcim USA, wet kiln).

NO<sub>x</sub> increased by about 25% with petcoke with a thermal energy change from 40% to 75%

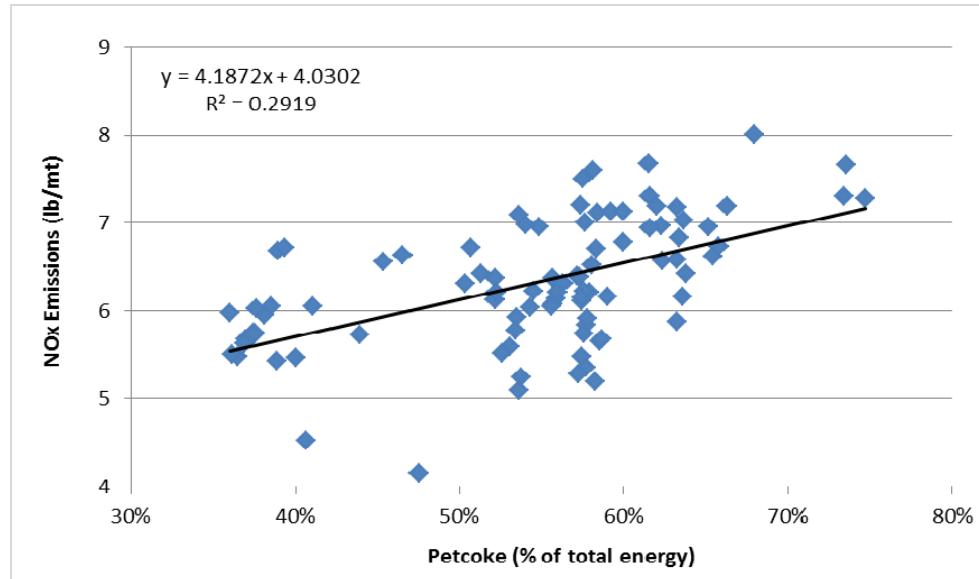


Figure 63: Petcoke substitution rate vs. NO<sub>x</sub> emissions in Dundee (source: PPE Project – Joel Keene)

#### Petcoke trials in Midlothian (Holcim USA, PC kiln)

Max. 33% of the coal was replaced by petcoke. The trial results indicate insignificant impact of petcoke on the kiln NO<sub>x</sub>.

- Petcoke and bituminous oil ("Pitch") comparison in Merone (Holcim Italy, PC kiln)  
Reduction of about 500 mg NO<sub>x</sub>/Nm<sup>3</sup> @ 10% oxygen or more was observed when switching from petcoke to bituminous oil as the main fuel.
- Petcoke increase in Alberthaw (UK, non-Holcim SP kiln)  
130 ppm increase of the kiln inlet NO when petcoke in the fuel mix increased from 30% to 70% petcoke at the main burner.
- Lakheri (India, PC kiln)  
With a change from 100% coal to 100% petcoke at separate line calciner (100% petcoke in main burner in both cases), NO<sub>x</sub> emissions at calciner string increased from ~1300 mg/Nm<sup>3</sup> to ~2100 mg/Nm<sup>3</sup> at 10% O<sub>2</sub>.
- Chaibasa (India, PC kiln)  
In October 2012, ILC fuel was changed temporarily from coal to petcoke. The NO<sub>x</sub> emissions increased from ~1100 mg/Nm<sup>3</sup> to ~1900 mg/Nm<sup>3</sup> @ 10 % O<sub>2</sub>.
- St. Genevieve (USA, PC kiln)  
NO<sub>x</sub> is kept below 500 mg/Nm<sup>3</sup> @ 10% O<sub>2</sub> as long as the PC fuel is coal (high volatile matter). Replacing 50% of the calciner fuel by petcoke resulted in emissions >850 mg/Nm<sup>3</sup> (data 2010).

### 10.8.1.2 Measures to minimize NO<sub>x</sub> emissions

#### Primary measures

- Improvement of process stability  
Process optimization, high-level control, raw meal and fuel dosing improvement
- Improvement of kiln feed burnability  
LSF, SR, fineness
- Avoid over-burning of clinker  
Avoid a too low clinker free lime target or production below target
- Burner optimization  
If possible, reduce primary and transport air, reduce injection velocity, reduce momentum, adapt tip design - without adversely affecting operation and quality
- Finer grinding of petcoke
- Low NO<sub>x</sub> calciner (hot spot and zone of reducing conditions)

Adding of lump fuel or fuel with high volatile content (AFR) to fuel mix

- ① Meal split:  
**control of hot spot**
- ② Air split\*:  
**reducing conditions**  
\* Or main fuel bellow tertiary air connection
- ③ "MSC"/Staged fuel:  
**Additional "LowNO<sub>x</sub> burner"**  
**or (lumpy) AFR**

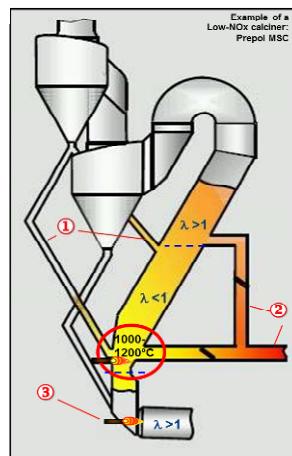


Figure 64: Concept of low NO<sub>x</sub> calciner<sup>1</sup> (source: Polysius)

#### Secondary measures

- Selective non-catalytic reduction SNCR: Reagent (ammonia) injection
- Selective catalytic reduction SCR

### 10.8.2 SO<sub>2</sub> emissions

Petcoke normally increases the sulphur input into the system. In general the sulphur scrubbing effect by raw meal in the preheater tower is very efficient, i.e. no sulphur from fuel contributes to SO<sub>2</sub> emissions out of preheater and pre-calciner kilns. Furthermore, there is absorption in the conditioning tower and in the raw mill during compound operation.

In modern kiln systems without bypass, SO<sub>2</sub> in the stack is therefore arising from the raw material (mainly pyrite) and not from the fuel.

<sup>1</sup> MSC = Multi-stage combustion

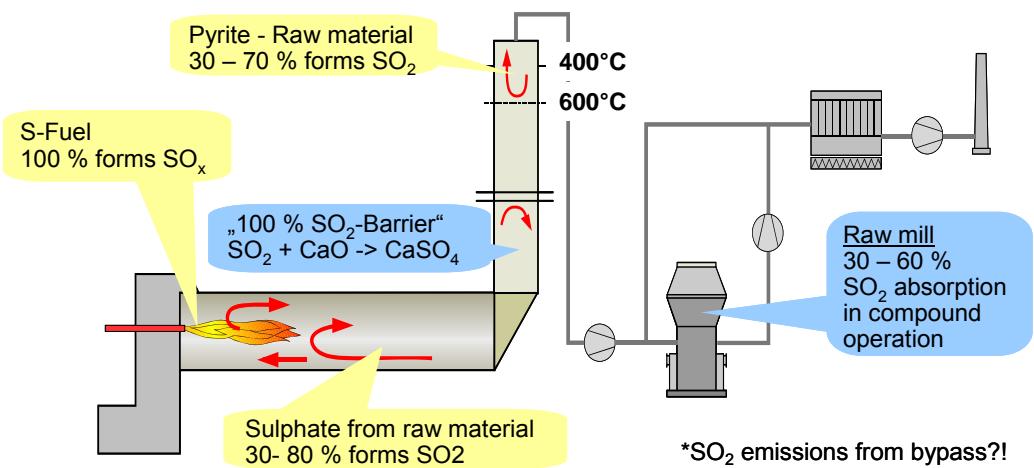


Figure 65: SO<sub>2</sub> formation and absorption in dry process with cyclone preheater

At very low excess air, the barrier may not be 100% efficient. Also if the change of fuel (sulphur content and ash) entails adjustments of the raw mix, the SO<sub>2</sub> situation can change. The required changes in the operation may further influence the raw material sulfur incorporation rate in the top stages (influenced by temperature, gas velocities etc.).

SO<sub>2</sub> emissions increase by petcoke is also expected in case of preheater and pre-calciner kiln systems equipped with a gas bypass, where the highly enriched kiln gases bypass suspension preheater, conditioning tower and raw mill, all of which have the "scrubbing" effect. The absorption potential of the bypass dust very much depends on operational conditions like the bypass dust amount (extraction design), gas conditioning, etc.

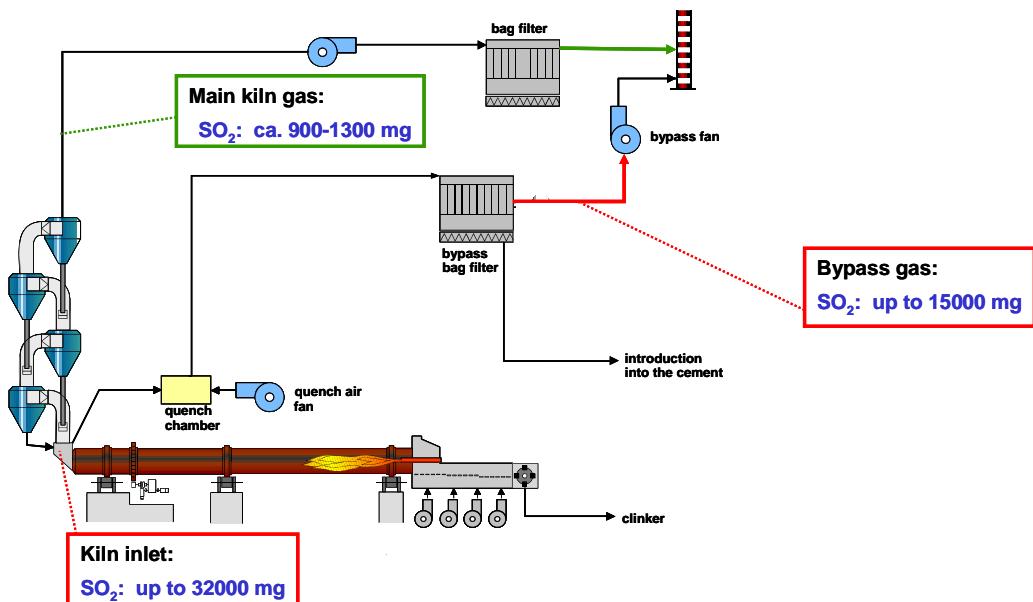


Figure 66: SO<sub>2</sub> concentrations (mg/Nm<sup>3</sup>) in a kiln system with kiln gas bypass

LEPOL kilns (grate preheater) offer some scrubbing effect, while scrubbing efficiency is less effective in long dry kilns. The lowest absorption is observed in wet kiln lines. An increase in SO<sub>2</sub> emissions is therefore expected in these kiln systems. The emissions depend on the burning conditions (sulphur volatility).

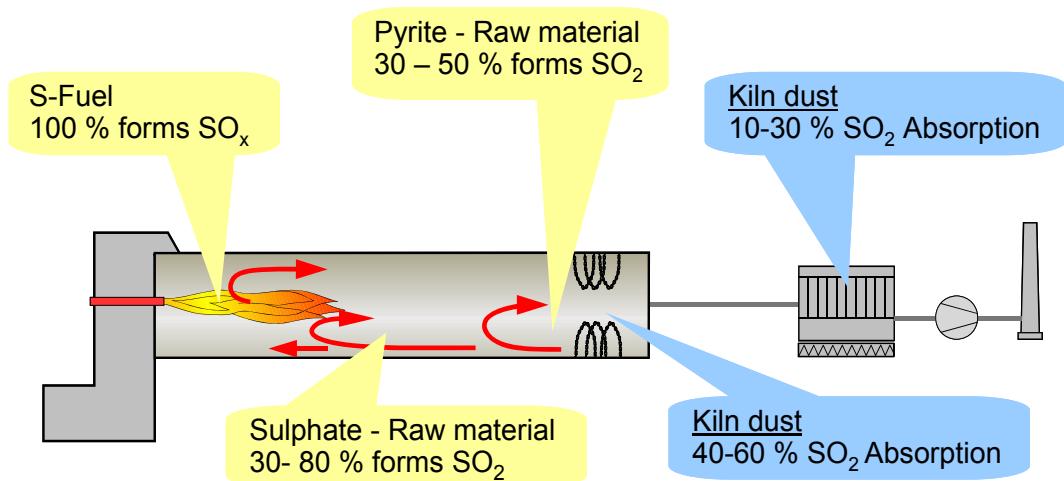


Figure 67: SO<sub>2</sub> formation and absorption in long kiln process (dry or wet)

Sulphur emissions from fuel are furthermore increased during start-up when no meal is scrubbing the SO<sub>2</sub>. Legal regulations have to be checked very carefully.

#### 10.8.2.1 Experiences

- Petcoke increase in Dundee (Holcim USA, wet kiln)  
SO<sub>2</sub> emissions went up by 7% when petcoke utilisation increased from 50% to 70%
- Petcoke implementation in Guayaquil (Holcim Ecuador, PC kiln w/o bypass)  
Based on Figure , it cannot be clearly concluded if there was any change in the SO<sub>2</sub> emissions.

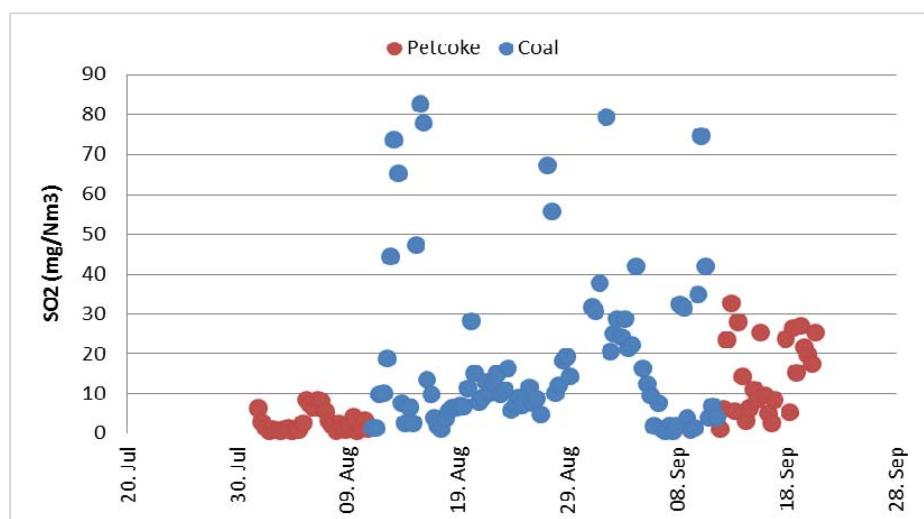


Figure 68: SO<sub>2</sub> emissions at Guayaquil (2009 data for kiln 1)

#### 10.8.2.2 Measures

##### Primary measures

- Prevention of increased sulphur volatility, mainly for long and Lepol kiln systems
  - Avoid combustion in reducing conditions
  - Avoid temperature peaks and over-burning
  - Avoid long flame (better to reduce residence time of material in hot zone, modernize burner to high momentum!)
  - Adjust alkali-sulfur ratio
  - Adjust burner position parallel to kiln axis
  - Optimize coke fineness and dispersion
  - Stable kiln operation
  - Improve burnability of kiln feed
- Exhaust gas cooling (the lower the main and bypass filter temperatures the higher the absorption of sulphur in the dust)
- Optimize raw mill runtime (absorption of sulphur on raw materials)

##### Secondary measures

- Injection of raw meal or dust into the mixing chamber of the bypass system
- Reagent like sodium bicarbonate or hydrated lime addition to kiln feed or injection into exhaust gas
- Wet scrubber

### 10.8.3 CO<sub>2</sub> emissions

The CO<sub>2</sub> emissions can be calculated from the emission factors in the following table (source: WBCSD<sup>1</sup> CO<sub>2</sub> Emissions Inventory Protocol, Version 3.04).

Type	Category	IPCC <sup>2</sup> default kg CO <sub>2</sub> /GJ	CSI <sup>3</sup> default kg CO <sub>2</sub> /GJ
<b>Fossil fuels</b>			
1	Bituminous coal, anthracite, waste coal	96	
2	Petcoke		92.8
3	(Ultra) heavy fuel	77.4	
4	Diesel oil	74.1	
5	Natural gas (dry)	56.1	
6	Oil shale	107	
6a	Lignite	101	
7	Gasoline	69.3	
<b>Alternative fuels</b>			
8	Waste oil	74	
9	Tyres	85	
10	Plastics	75	
11	Solvents	74	
12	Impregnated saw dust	75	
12a	Mixed industrial waste	83	
13	Other fossil-based fuels	80	
<b>Biomass fuels</b>			
14	Dried sewage sludge	110	
15	Wood, non-impregnated saw dust	110	
16	Paper, carton	110	
17	Animal meal	89	
18	Animal bone meal	89	
19	Animal fat	89	
20	Agricultural, organic, diaper waste, charcoal	110	
21	Other biomass	110	

The CO<sub>2</sub> emissions per GJ are lower for petcoke in comparison to coal. As long as there is no increase in heat consumption, the cement specific CO<sub>2</sub> emissions are lowered by switching to petcoke.

However there can be indirect effects on CO<sub>2</sub> e.g. increased electrical power demand of the cement mill due to increased grinding efforts with less gypsum in cement, higher pressure drop in preheater due to the higher oxygen requirement inside the kiln, etc.

<sup>1</sup> WBCSD = World Business Council for Sustainable Development

<sup>2</sup> IPCC = International Panel on Climate Change

<sup>3</sup> CSI = Cement Sustainability Initiative of WBCSD

#### 10.8.3.1 Experiences

- Petcoke implementation in Guayaquil (Holcim Ecuador, PC kiln)  
Considering only the fuel consumption, there was a slight decrease in CO<sub>2</sub> emissions (from 307 kg CO<sub>2</sub>/t<sub>cli</sub> to 297 kg CO<sub>2</sub>/t<sub>cli</sub>).

#### 10.8.3.2 Measures

- Reduction of energy consumption
- Decrease clinker factor in cement

### 10.8.4 Other emissions

#### 10.8.4.1 Heavy metals

As the emission-relevant heavy metals (highly volatile like mercury and thallium) in petcoke are usually much less than coal, such emissions generally tend to decrease with the use of petcoke.

Vanadium and nickel on the other hand can be 10 or more times higher in petcoke. However these components are less emission-relevant due to their low volatility and the level in the stack is in general far below limits even with a high input. Attention must be paid if the kiln system is equipped with a bypass (handling of dust accumulated with heavy metals).

#### 10.8.4.2 CO emissions

Since petcoke is more difficult to burn in comparison to coal, the CO level can increase. However, operational measures to enhance combustion performance shall prevent CO formation or CO surviving up to the stack. Especially in calciners with low residence time, there is however a risk of higher CO emissions.

#### 10.8.4.3 Dust emissions

Although kiln is dustier with petcoke, dust emissions hardly change with a change from coal to petcoke. Modern bag filters are able to achieve clean gas contents of below 20 mg/Nm<sup>3</sup> in any case.

Electrostatic precipitators (EP) are more sensitive to operational changes (e.g. temperature). Due to safety reasons, EP has to be stopped at high CO level (peaks) which can result in higher dust emissions from the stack.

#### 10.8.4.4 HCl emissions

Basically the same effect as from SO<sub>2</sub>, however petcoke generally has less Cl than in coal.

## Annex 1: Holcim plants using petcoke (ATR 2012)

Abbr.	Plant	Country	Kiln ident	Kiln BDP	Kiln type	Process type	Petcoke %S
A1	Ambuja Nagar 1	India	A1-1	4'580	PC6	D	5.36
A2	Ambuja Nagar 2	India	A2-1	4'580	PC6	D	
			A2-3	4'580	PC6	D	
AC	Acapulco	Mexico	AC-1	1'185	PC4	D	6.86
AD	Ada	USA	AD-1	840	WL	W	5.05
			AD-2	840	WL	W	
AE	Alesd	Romania	AE-1	4'300	PC4	D	1.97
AL	Altkirch	France	AL-4	1'320	DS4	D	2.44
AP	Apaxco	Mexico	AP-1	2'880	DS4	D	3.31-5.48
			AP-2	2'880	DS4	D	
B1	Bhatapara 1	India	B1-1	3'900	PC4	D	6.50
B2	Bhatapara 2	India	B2-1	7'000	PC6	D	
BE	Beli Izvor	Bulgaria	BE-1	3'300	PC5	D	1.82
BO	Barroso	Brazil	BO-1	2'000	DS4	D	4.59
CA	Capdeville	Argentina	CA-1	2'078	DS4	D	NAV
CG	Cartago	Costa Rica	CG-2	2'520	PC5	D	NAV
CP	Campulung	Romania	CP-4	4'000	PC5	D	5.35
CS	Carboneras	Spain	CS-1	3'416	DS4	D	5.20
CT	Cantagalo	Brazil	CT-1	1'134	DS4	D	4.61
CW	Chekka White Cement	Lebanon	CW-2	280	DL	D	4.48
DL	Darlaghat	India	DL-1	7'768	PC6	D	5.89
DN	Dannes	France	DN-6	1'272	DG	SW	4.76
EC	Eclépens	Switzerland	EC-3	2'300	PC4	D	3.03
ER	El Ronco	El Salvador	ER-5	2'520	PC5	D	3.55
FE	Fès	Morocco	FE-1	1'400	DS5	D	4.86
G1	Gagal 1	India	G1-1	4'300	PC6	D	5.56
G2	Gagal 2	India	G2-2	4'950	PC6	D	
GA	Gador	Spain	GA-1	2'320	DS4	D	6.03
GU	Guayaquil	Ecuador	GU-1	3'078	PC5	D	NAV
			GU-2	3'078	PC5	D	
GV	Ste. Genevieve	USA	GV-1	12'000	PC5	D	5.11
HE	Héming	France	HE-1	1'148	DG	SD	4.40
			HE-3	1'148	DG	SD	
HR	Hermosillo	Mexico	HR-1	3'500	PC6	D	4.43
JE	Jerez de la Frontera	Spain	JE-1	2'256	DS4	D	4.86
JL	Jamul	India	JL-1	600	DG	SD	NAV

			JL-2	600	DG	SD	
Abbr.	Plant	Country	Kiln ident	Kiln BDP	Kiln type	Process type	Petcoke %S
			JL-3	600	PC5	D	NAV
JO	Joliette	Canada	JO-1	726	DL	D	NAV
			JO-2	726	DL	D	
			JO-3	726	DL	D	
			JO-4	726	DL	D	
KO	Koromacno	Croatia	KO-1	1'675	DS4	D	3.54
LA	Lábatlan	Hungary	LA-5	438	WL	W	3.02
LK	Lakheri	India	LK-1	3'200	PC7	D	5.80
LO	Lorca	Spain	LO-1	1'908	DS2	D	NAV
LU	Lumbres	France	LU-4	778	WL	W	5.54
			LU-5	778	WL	W	
ME	Merone	Italy	ME-4	2'500	PC4	D	4.30
MG	Malagueño	Argentina	MG-2	1'400	PC5	D	NAV
MI	Mississauga	Canada	MI-3	4'450	PC4	D	5.72
MK	Madukkarai	India	MK-1	2'435	PC4	D	NAV
ML	Midlothian	USA	ML-2	3'450	PC4	D	5.40
MP	Macuspana	Mexico	MP-1	2'700	PC4	D	NAV
NP	Novi Popovac	Serbia	NP-1	2'200	DS4	D	5.46
OB	Obourg	Belgium	OB-10	2'640	WL	W	4.82
			OB-9	2'640	WL	W	
OJ	Oujda	Morocco	OJ-1	2'236	DS4	D	NAV
			OJ-2	2'236	DS4	D	
OZ	Orizaba	Mexico	OZ-2	1'720	DS4	D	NAV
			OZ-3	1'720	PC4	D	
PD	Portland	USA	PD-4	5'237	PC5	D	2.58
PL	Pedro Leopoldo	Brazil	PL-1	2'845	DS4	D	5.44
			PL-2	2'845	DS4	D	
PO	Polpaico	Chile	PO-1	1'950	DS4	SW	2.17
RA	Ramos Arizpe	Mexico	RA-2	3'150	PC6	D	NAV
RB	Rabriyawas	India	RB-1	6'000	PC6	D	6.65
RF	Rochefort	France	RF-1	1'270	DG	SD	3.41
RN	Rohoznik	Slovak Republic	RN-3	3'780	PC5	D	3.03
RU	Rauri	India	RU-1	7'000	PC5	D	5.98
RW	Rohoznik White Cement	Slovak Republic	RW-1	490	DS3	D	3.03
SA	Settat	Morocco	SA-1	4'000	PC5	D	6.10
SM	San Miguel	Guatemala	SM-61	1'245	DS4	D	NAV
			SM-62	1'245	DS4	D	
			SM-63	1'245	PC5	D	
TC	Tecomán	Mexico	TC-1	3'020	PC4	D	4.11-5.74

			TC-2	3'020	PC4	D	
Abbr.	Plant	Country	Kiln ident	Kiln BDP	Kiln type	Process type	Petcoke %S
TE	Ternate	Italy	TE-3	2'850	PC5	D	4.04
TH	Theodore	USA	TH-1	4'850	PC4	D	5.67
TR	Trident	USA	TR-5	907	WL	W	5.30
W2	Wadi 2	India	W2-1	12'500	PC6	D	NAV
YE	Yeles	Spain	YE-1 YE-2	998 998	DS4 SH1	D D	5.91
YO	Yocsina	Argentina	YO-2	1'750	DS4	D	NAV

NAV = Not available

## Annex 2: Petcoke guidelines

### What is different to coal?

Compared to coal, petcoke requires special attention in following areas:

Blending	✓ Uniform blending with raw coal (if petcoke < 100%)
Grinding	✓ Higher fineness (less volatiles) ✓ Affects mill capacity (different grindability, higher fineness)
Burning	✓ Low ash and high CV ✓ Delayed ignition (low reactivity) ✓ High sulfur causes more plugging (kiln inlet, preheater) ✓ Stable and controlled kiln process necessary to minimize sulfur cycles
Clinker quality	✓ More SO <sub>3</sub> in clinker (better early strength, reduced gypsum addition)

### What are the guidelines?

For a first "conservative" approach, go for the following targets<sup>1</sup>:

SO<sub>3</sub> in clinker < 1.5%, Molar A/S > 0.8

The following limits are based on best practices within Holcim (source: ATR 2004):

Kiln system	Min. Alk/SO <sub>3</sub> ratio	Max. sulfur in clinker %SO <sub>3</sub> cli
PC – Pre-calciner	0.4	2.0
SP – Suspension preheater	0.5	1.7
DL – Long, dry	0.8	1.2
DG – Grate preheater (Lepol)	0.8	1.0
WL – Long, wet	0.8	1.0

Petcoke supply	✓ Choose quality that fits into the given restrictions for sulfur input and grinding capacity. Choosing a good quality (<5% S and >55 HGI) is not necessarily the optimum cost option <sup>2</sup> .
Raw coal/petcoke preparation	✓ Controlled mixing from two feed hoppers
Grinding	✓ Recommended fineness: <div style="border: 1px solid black; padding: 5px; text-align: center;"><math display="block">\text{Residue on } 90 \mu\text{m} \leq [(\text{Coal} \cdot 0.5 \cdot VM) + (\text{Petcoke} \cdot 5)]/100</math></div>

<sup>1</sup> "Conservative" is relative. On SP/PC kilns, 2.5% SO<sub>3</sub> input and 0.4 A/S have been achieved through an aggressive approach. However, certain factors act against high sulfur incorporation e.g. lump fuel (AFR) which reaches the material bed, long kilns or grate preheater kilns.

<sup>2</sup> Burning high grade petcoke (<5% S, >55 HGI) as recommended in the past would be easier but the market for such a quality stagnates (due to higher prices) over a period of time. A more aggressive approach towards petcoke (6-7% S, <40 HGI) provides higher savings.

where,  
 Coal = Portion of coal in fuel mix, mass%  
 VM = Volatile matter in coal, mass%  
 Petcoke = Portion of petcoke in fuel mix, mass%

- ✓ Uniformity of fineness:  $\text{CoV} (R 90\mu) < 5\%$
- ✓ Determine mill output by trial (HGI can be misleading, greasing effect)

Kiln feed	Uniformity	<ul style="list-style-type: none"> <li>✓ Short-term kiln feed fluctuations (hourly samples)                     <math>\text{STD}_{\text{LSF}} &lt; 1.2^1</math>  <math>\text{STD}_{\text{SR}} &lt; 0.04</math>  <math>\text{STD}_{\text{AR}} &lt; 0.04</math> </li> </ul>
Burnability		<ul style="list-style-type: none"> <li>✓ Good burnability helps (if there is a low-cost possibility to improve it<sup>2</sup>). Assessment methods:                     <ul style="list-style-type: none"> <li>- Holcim Burnability Model (by HTEC/CM-MT)</li> <li>- Combinability Temperature (guide value for 100% high sulfur petcoke &lt; 1450°C, max. 1500°C)</li> </ul> </li> </ul>
		$CT = 436 + 21 \cdot AIR_{90\mu_{KF}} + 10 \cdot LSF_{cli} + 3 \cdot R_{150\mu_{KF}} + 32 \cdot AR_{cli} - 250 \cdot F_{cli} - 20 \cdot SO_3_{cli}$
Dosing		<ul style="list-style-type: none"> <li>✓ Short term quantity fluctuations (10 s) &lt; 1 %</li> </ul>
Fine coal dosing		<ul style="list-style-type: none"> <li>✓ Short term fluctuations (10 s) &lt; 1 %</li> <li>✓ Fluctuations in CV &lt; 1% (coal/petcoke)</li> <li>✓ Pressure fluctuations in transport duct (at burner) &lt; 10%</li> <li>✓ Conveying duct &lt; 80 m, velocity 28-35 m/s</li> <li>✓ Diverting pots instead of bends recommended</li> </ul>
Kiln	Burner & flame	<ul style="list-style-type: none"> <li>✓ Use high momentum burner (new burner 11 N/MW, existing burner 9-11 N/MW) for compact and short flame. For a given burner / PA fan (with limited operating range), adjust burner for most compact and shortest flame i.e. max. primary air quantity and pressure, max. radial air, retract burner).</li> </ul>

<sup>1</sup> Standard  $\text{STD}_{\text{LSF}}$  target of optimized kilns. However, even if this target is unachieved, plants can still incorporate higher sulfur e.g. Midlothian plant operates with 4.4  $\text{STD}_{\text{LSF}}$ , but 1.34 %  $\text{SO}_3$  in clinker!

<sup>2</sup> Mineralizers (F) would help to incorporate  $\text{SO}_3$ . However mineralizers so far have been used with simultaneous increase of LSF to improve the clinker quality. Experience at constant LSF is rare (FLS mineralization tests at Siggenthal plant).

- ✓ In particular, retracting burner tip on grate cooler kilns can have a strong positive impact<sup>1</sup>.
  - ✓ Burner orientation in line with kiln axis
  - ✓ Petcoke injection velocity = 20-25 m/s
- Cooler
- ✓ Stable and high secondary air temperature for stable ignition (cooler optimization)
- O<sub>2</sub>/CO
- ✓ Gas analysis at kiln inlet mandatory (ILC)
  - ✓ Kiln inlet O<sub>2</sub> = 2-3 %, CO < 0.05% (< 500 ppm) (in case of ILC kiln, higher O<sub>2</sub> of 4-5% is acceptable; however disadvantage could be lower flame temperature and higher kiln inlet temperature)
- Monitoring
- ✓ Monitor free lime
  - ✓ Monitor kiln shell temperature profile (flame shape)
- Granulometry
- ✓ As a consequence of higher SO<sub>3</sub>, clinker tends to be finer (impact on grate cooler). If necessary, adjust clinker SR/AR to alleviate effects of finer clinker.
- Pre-calciner
- ✓ Hot flame core for stable ignition ("Hot Spot")
  - ✓ Combustion in pure air better than with kiln gas (ILC, pre-combustion chamber)
- Retention time
- ✓ The following gas retention time guidelines could be used (if not possible, increase petcoke fineness):
- | Fuel            | ILC, s | SLC, s |
|-----------------|--------|--------|
| Petcoke         | 4      | 3      |
| Bituminous coal | 3      | 2      |
| Lignite         | 3.5    | 2.5    |
- Burn out
- ✓ After calciner, O<sub>2</sub> = 2-3%, CO < 0.05 % (< 500 ppm); after PH, 1% higher O<sub>2</sub> due to false air). Check out hot meal for combustibles (sparkling).
- Dust curtain
- ✓ Dust curtain kiln inlet: <20-30% meal from 2<sup>nd</sup> lowest stage to kiln inlet (splash box!). If no pre-calciner, dust curtain in riser duct by lowering meal entry points.
- Hot meal analysis
- ✓ Adequate frequency, usually once/shift (LOI, SO<sub>3</sub>, K<sub>2</sub>O). SO<sub>3</sub> < 5% (if chlorine < 0.5%)
- Bypass
- ✓ An existing bypass alleviates the sulfur cycles, but installation of a new bypass can hardly be justified by the use of petcoke. Fight SO<sub>3</sub> cycles by enhanced preheater cleaning.

---

<sup>1</sup> For example, Chekka plant retracted burner by 1.1 m out of the kiln which increased SO<sub>3</sub> in clinker from 0.6% to 1.3%. However, retracting a burner could result in hotter kiln outlet and formation of snowman in cooler.

#### Preheater cleaning

- ✓ Add poke holes and install air cannons (could be up to 60) where coatings occur. Removal of heavy blockages can also be done with CARDOX blasting on demand. Special attention required for calciner orifice (restriction); if restricted by build-ups, the problem will self-accelerate rapidly due to lack of O<sub>2</sub>.
- Recommendation:** Use coating-repellent SiC refractory in the riser duct.

#### How to proceed?

- ✓ Stepwise increments of petcoke use, based on process and quality data. Depending on results, further stretch the preliminary limits for SO<sub>3</sub> input and Alk/SO<sub>3</sub> ratio.

**Know your process!**

## Annex 3: Petcoke community on iShare



### Documents

- Firing (field experiences about burning of petcoke)
- Grinding (field experiences about grinding of petcoke)
- Market (information on current market situation)
- Progress (summary of petcoke utilisation in Holcim)
- Tools (collection of guides, spreadsheets, reports, etc.)

Petcoke Community on iShare was revamped in November 2012 and now offers a **Forum** to exchange knowledge and share practical experience.

**Petcoke Community**

**Objective**

The aim of the "Petcoke Community" is to foster the exchange of experiences between HGRS and the group plants to develop best practices and guidelines for successful utilization of petcoke.

**Events**

Contains information about past 'AFR and Petcoke Turntable' as well as details about future courses / seminars

In certain regions, petcoke has the price advantage compared to other fuels and therefore helps to reduce thermal energy costs. Availability, handling, grinding and combustion issues is potential benefit from the petcoke.

**Latest News**

Progress is on track. The 1st version of the manual shall be released in January 2013.

**Members**

List of all members registered on Petcoke Discussion Forum

**Forum: Petcoke**

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Messages: 14 - Threads: 2 - Filter: All Threads

Thread	Author	Views	Replies	Last Post
filter media types in petcoke mill grinding	Berrios, Gustavo	92	1	Dec 3, 2012 4:21 PM Last Post By: Weber, Mirko »
Petcoke & NOx emissions from Separate Line Calciner	More, Satesh	256	11	Nov 26, 2012 7:21 PM Last Post By: More, Satesh »

**Search Forum**

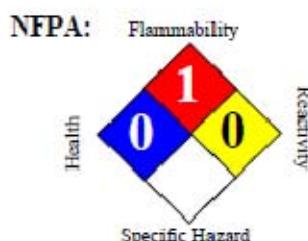
- ✓ By the end of 2012, over 70 members had registered on the forum with participation from,
  - OPCOs (where petcoke is one of the fuels)
  - HTEC (TPT, MPT, MT, PROC<sup>1</sup>)
  - RMSOs
  - HTR<sup>2</sup>
- ✓ Forum is open to all iShare users with 'read' access. 'Write' access is validated only for the forum members to ensure good quality of the feedback / contribution.
- ✓ Please contact [torsten.seidler@holcim.com](mailto:torsten.seidler@holcim.com) if you wish to become a member.

<sup>1</sup> Procurement

<sup>2</sup> Holcim Trading

## Annex 4: OH&S issues with petcoke

### Safety Data Sheet Petroleum Coke



#### SECTION 1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	Petroleum Coke			
Synonyms	:	Green Coke, Uncalcined Coke, Thermocracked Coke, Fuel Grade Coke, 888100004472			
SDS Number	:	888100004472	Version	:	1.20
Product Use Description	:	Fuel			
Company	:	For: Tesoro Refining & Marketing Co. 19100 Ridgewood Parkway, San Antonio, TX 78259			
Tesoro Call Center	:	(877) 783-7676	Chemtrec (Emergency Contact)	:	(800) 424-9300

#### SECTION 2. HAZARDS IDENTIFICATION

Classifications	:	Combustible Dust
Pictograms	:	None
Signal Word	:	WARNING
Hazard Statements	:	May form combustible dust concentrations in air. Excessive exposure may cause skin, eye or respiratory tract irritation.
Precautionary Statements		
Prevention		Avoid accumulations of finely ground dust. Keep away from flames and hot surfaces. No smoking. Wear gloves, eye protection and face protection as needed to prevent skin and eye contact with liquid. Wash hands or liquid-contacted skin thoroughly after handling. Do not eat, drink or smoke when using this product. Do not breathe dust. Use only outdoors or in a well-ventilated area.
Response		In case of fire: Use dry chemical, CO <sub>2</sub> , water spray or fire fighting foam to extinguish. If on skin (or hair): Rinse skin with water or shower. Remove and wash contaminated clothing. If in eye: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If inhaled: Remove person to fresh air and keep comfortable for breathing.

Storage	Immediately call or doctor or emergency medical provider. If skin, eye or respiratory system irritation persists, get medical attention.
Disposal	Avoid generating heavy concentrations of airborne, finely-ground petroleum coke dust. Avoid accumulations of finely ground dust on surfaces of equipment or buildings.
Disposal	Dispose of contents/containers to approved disposal site in accordance with local, regional, or national regulations.

### SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Component	CAS-No.	Weight %
Coke (Petroleum)	64741-79-3	100%

### SECTION 4. FIRST AID MEASURES

Inhalation	: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If necessary, provide additional oxygen once breathing is restored if trained to do so. Seek medical attention immediately.
Skin contact	: Take off all contaminated clothing immediately. Wash off with soap and plenty of water. Wash contaminated clothing before re-use. Seek medical advice if symptoms persist or develop.
Eye contact	: Remove contact lenses. Immediately flush eyes thoroughly with warm water for at least 15 minutes. Hold the eyelids open and away from the eyeballs to ensure that all surfaces are flushed thoroughly. Seek medical advice.
Ingestion	: Ingestion is considered unlikely. However, inhalation procedures should be followed if this happens. Drink 1 or 2 glasses of water. Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Obtain medical attention.
Notes to physician	: Symptoms: Vomiting, Diarrhea, Pain

### SECTION 5. FIRE-FIGHTING MEASURES

Suitable extinguishing media	: Water spray, Dry chemical, Foam, Carbon dioxide blanket, A solid stream of water may scatter and spread the fire.
Specific hazards during fire fighting	: Product will burn. In very large quantities, spontaneous heating and combustion may occur. Fire will produce dense black smoke containing hazardous combustion products (see Section 10).
Special protective equipment for fire-fighters	: Firefighting activities that may result in potential exposure to high heat, smoke or toxic by-products of combustion should require NIOSH/MSHA- approved pressure-demand self-contained breathing apparatus with full facepiece and full protective clothing.
Further information	: Large fires are best extinguished with water. Surfactant (foam or soap) in water may be effective in reaching deep, smoldering fires (such as in coke pile).

### SECTION 6. ACCIDENTAL RELEASE MEASURES

**SAFETY DATA SHEET****Petroleum Coke**

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Personal precautions	: ACTIVATE FACILITY'S SPILL CONTINGENCY OR EMERGENCY RESPONSE PLAN if applicable. Ventilate the area. Evacuate personnel to safe areas.
Environmental precautions	: Prevent further leakage or spillage. Should not be released into the environment. Do not allow material to contaminate ground water system. In case of accident or road spill notify CHEMTRIC (800) 424-9300. U.S. Coast Guard regulations require immediate reporting of spills that could reach any waterway including intermittent dry creeks. Report spill to Coast Guard toll free number (800) 424-8802.
Methods for cleaning up	: Carefully vacuum, shovel, scoop or sweep up into a waste container for reclamation or disposal. Water fog may be necessary to minimize dust generation. Respiratory protection is recommended where visible dust may be generated.

**SECTION 7. HANDLING AND STORAGE**

Precautions for safe handling	: Minimize physical contact with the product. Avoid conditions which create dust. Do not breathe vapors or dust. Avoid dispersal of coke dust into air such as cleaning dusty surfaces with compressed air.  : Keep away from heat and sources of ignition. No smoking near areas where material is stored or used. Ground and bond containers during product transfers to reduce the possibility of static-initiated fire or explosion.
Dust explosion class	: High concentrations of airborne petroleum coke dusts may be ignited by contact with heated surface. Airborne coke dust is primarily a fire hazard, but explosion may be possible.
Conditions for safe storage, including incompatibilities	: Avoid generation and accumulation of dust when handling this material. Refer to NFPA 654 Standard for Prevention of Fire & Dust Explosions.  : Stable under recommended storage conditions.

**SECTION 8. EXPOSURE CONTROLS / PERSONAL PROTECTION****Exposure Guidelines**

List	Components	CAS-No.	Type:	Value
OSHA	Petroleum Coke	64741-79-3	TWA	15 mg/m <sup>3</sup> (total dust) 5 mg/m <sup>3</sup> (respirable dust)
ACGIH	Petroleum Coke	64741-79-3	TL	10 mg/m <sup>3</sup> (total dust) 3 mg/m <sup>3</sup> (respirable dust)
OSHA	Coal Tar Pitch Volatiles Benzene Soluble Fraction	65996-93-2	TWA	0.2 mg/m <sup>3</sup>
ACGIH	Coal Tar Pitch Volatiles Benzene Soluble Fraction	65996-93-2	TLV	0.2 mg/m <sup>3</sup>

NOTE: Limits shown for guidance only. Follow applicable regulations.

Engineering measures	: Use adequate ventilation to keep dust concentrations of this product below occupational exposure limits. Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Dust control equipment such as local exhaust ventilation or material transport systems handling coke should contain explosion relief vents or explosion suppression systems.
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<b>Eye protection</b>	: Indirect vented, dust-tight goggles are recommended if dust is generated when handling this product.
<b>Hand protection</b>	: Work gloves are recommended if needed to prevent repeated or prolonged skin contact.
<b>Skin and body protection</b>	: Disposable clothing such as Tyvek® (DuPont) may be warranted to minimize skin and clothing contamination, depending on the work to be performed. Flame resistant clothing such as Nomex ® is recommended in areas where material is stored or handled.
<b>Respiratory protection</b>	: A NIOSH/ MSHA-approved air-purifying respirator with particulate classification N-95 or greater filter cartridges or canister may be permissible under certain circumstances where airborne concentrations are or may be expected to exceed exposure limits or for odor or irritation. Protection provided by air-purifying respirators is limited. Refer to OSHA 29 CFR 1910.134, ANSI Z88.2-1992, NIOSH Respirator Decision Logic, and the manufacturer for additional guidance on respiratory protection selection. Use a NIOSH/ MSHA-approved positive-pressure supplied-air respirator if there is a potential for uncontrolled release, exposure levels are not known, in oxygen-deficient atmospheres, or any other circumstance where an air-purifying respirator may not provide adequate protection.
<b>Hygiene measures</b>	: Use good personal hygiene practices. Avoid repeated and/or prolonged skin exposure. Wash hands before eating, drinking, smoking, or using toilet facilities. When using do not eat, drink or smoke. Promptly remove contaminated clothing and launder before reuse.

**SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES**

<b>Appearance</b>	Dark brown to black solid
<b>Odor</b>	Asphalt – like odor
<b>Odor threshold</b>	Not determined
<b>pH</b>	Not determined
<b>Melting point/freezing point</b>	Not determined
<b>Initial boiling point</b>	Not determined
<b>Flash point</b>	Not determined
<b>Evaporation rate</b>	Not determined
<b>Flammability (solid, gas)</b>	Solid
<b>Upper flammable limit</b>	Not determined
<b>Lower flammable limit</b>	15 to 1000 g/m³
<b>Vapor Pressure</b>	Not applicable
<b>Vapor density (air = 1)</b>	No data available
<b>Relative density (water = 1)</b>	>1.0
<b>Solubility (in water)</b>	Insoluble
<b>Partition coefficient (n-octanol/water)</b>	No data available

Auto-ignition temperature	670°C (1,238°F)
Kinematic viscosity	No data available
Kst	47 to 74 lbar m/s
MIE	> 1000 mj

## SECTION 10. STABILITY AND REACTIVITY

Reactivity	: Airborne dust may become flammable or explosive.
Chemical stability	Stable under normal conditions.
Possibility of hazardous reactions	Keep away from oxidizing agents, and acidic or alkaline products.
Conditions to avoid	Avoid accumulation of finely ground dust. Minimize generation of airborne dust. See Section 7 for additional information.
Hazardous decomposition products	In case of fire, hazardous decomposition products may be produced such as carbon monoxide, carbon dioxide, hydrocarbons and smoke. No decomposition if stored and applied as directed.

## SECTION 11. TOXICOLOGICAL INFORMATION

Inhalation	Inhalation of excessive dust concentrations may be irritating to the upper respiratory system. Repeated chronic inhalation exposure may cause impaired lung function. There is no evidence that such exposures cause pneumoconiosis, carcinogenicity, or other chronic health effects.
Ingestion	Low order of oral toxicity. Ingestion is considered unlikely. However, good personal hygiene such as washing hands and face after handling or contacting material before eating, drinking or smoking should be practiced to minimize ingestion of this product.
Skin contact	Contact may cause skin irritation.
Eye contact	May cause irritation, experienced as mild discomfort and seen as slight excess redness of the eye.
Further information	Repeated inhalation of the petroleum coke dust (10.2 and 30.7 mg/m <sup>3</sup> ) over a two-year period resulted in lung damage typical of high dust exposure including inflammation and scarring in rats. Similar exposures in monkeys did not produce similar lung effects. There was no observation of a carcinogenic effect at any dose following a lifetime exposure. There is no evidence of pneumoconiosis or carcinogenicity in human health studies. 24 months of exposure in monkeys and rats to either 10.2 or 30.7 mg/m <sup>3</sup> of coke dust resulted in lung accumulation of dust. There was no associated tissue abnormality in monkeys. A low level inflammatory response developed in the rat lung at 10.2 mg/m <sup>3</sup> and more significant inflammatory changes occurred in the rat lung at 30.7 mg/m <sup>3</sup> . There was no evidence of carcinogenicity in either species. Mouse skin painting bioassay negative.
Acute oral toxicity	LD50 rat Dose: > 2,000 mg/kg The toxicological data has been taken from products of similar composition.
Acute dermal toxicity	LD50 rabbit Dose: > 2,000 mg/kg The toxicological data has been taken from products of similar composition.

Acute inhalation toxicity	No data available
<b>Carcinogenicity</b>	
NTP	No component of this product which is present at levels greater than or equal to 0.1 % is identified as a known or anticipated carcinogen by NTP.
IARC	No component of this product which is present at levels greater than or equal to 0.1 % is identified as probable, possible or confirmed human carcinogen by IARC.
OSHA	No component of this product which is present at levels greater than or equal to 0.1 % is identified as a carcinogen or potential carcinogen by OSHA.
CA Prop 65	This product does not contain any chemicals known to State of California to cause cancer, birth, or any other reproductive defects.

## SECTION 12. ECOLOGICAL INFORMATION

Additional ecological information	: Keep out of sewers, drainage areas, and waterways. Report spills and releases, as applicable, under Federal and State regulations.
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## SECTION 13. DISPOSAL CONSIDERATIONS

Disposal	: Dispose of container and unused contents in accordance with federal, state and local requirements. Product is suitable for burning for fuel value in compliance with applicable laws and regulations. RCRA: The unused product, in our opinion, is not specifically listed by the EPA as a hazardous waste (40 CFR, Part 261D), nor is it formulated to contain materials which are listed hazardous wastes. It does not exhibit the hazardous characteristics of ignitability, corrosivity, or reactivity. The unused product is not formulated with substances covered by the Toxicity Characteristic Leaching Procedure (TCLP). However, used product may be regulated.
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## SECTION 14. TRANSPORT INFORMATION

CFR	: Not regulated by USA DOT 49 CFR.
ICAO/IATA	: Not regulated by ICAO/IATA.

## SECTION 15. REGULATORY INFORMATION

### U.S. FEDERAL, STATE AND LOCAL REGULATORY INFORMATION

Any spill or uncontrolled release of this product, including any substantial threat of release, may be subject to federal, state and/local reporting requirements. This product and/or its constituents may also be subject to other regulations at the state and/or local level. Consult those regulations applicable to your facility/operation.

TSCA Status	: On TSCA Inventory
DSL Status	: All components of this product are on the Canadian DSL list.
SARA 311/312 Hazards	: No SARA Hazards

**CERCLA SECTION 103 and SARA SECTION 304 (RELEASE TO THE ENVIRONMENT)**

The CERCLA definition of hazardous substances contains a "petroleum exclusion" clause which exempts crude oil, fractions of crude oil, and products (both finished and intermediate) from the crude oil refining process and any indigenous components of such from the CERCLA Section 103 reporting requirements. However, other federal reporting requirements, including SARA Section 304, as well as the Clean Water Act may still apply.

PENN RTK

US. Pennsylvania Worker and Community Right-to-Know Law (34 Pa. Code Chap. 301-323)

ComponentsCAS-No.

Coke (Petroleum)

64741-79-3

NJ RTK

US. New Jersey Worker and Community Right-to-Know Act (New Jersey Statute Annotated Section 34:5A-5)

ComponentsCAS No.

Coke (Petroleum)

64741-79-3

California Prop. 65

: This product may contain detectable quantities of chemicals known to the State of California to cause cancer, birth defects or other reproductive harm, and which may be subject to the requirements of California Proposition 65.

Nickel / Nickel Compounds	Cancer	7440-02-0
Chromium, Hexavalent Compounds	Cancer	18540-29-9
Lead	Cancer	7439-92-1
Lead	Developmental	7439-92-1
Polycyclic Aromatic Hydrocarbons including:		
Benzo(a)pyrene	Cancer	50-32-8
Indeno(1,2,3-cd)pyrene	Cancer	193-39-5

**SECTION 16. OTHER INFORMATION**Further information

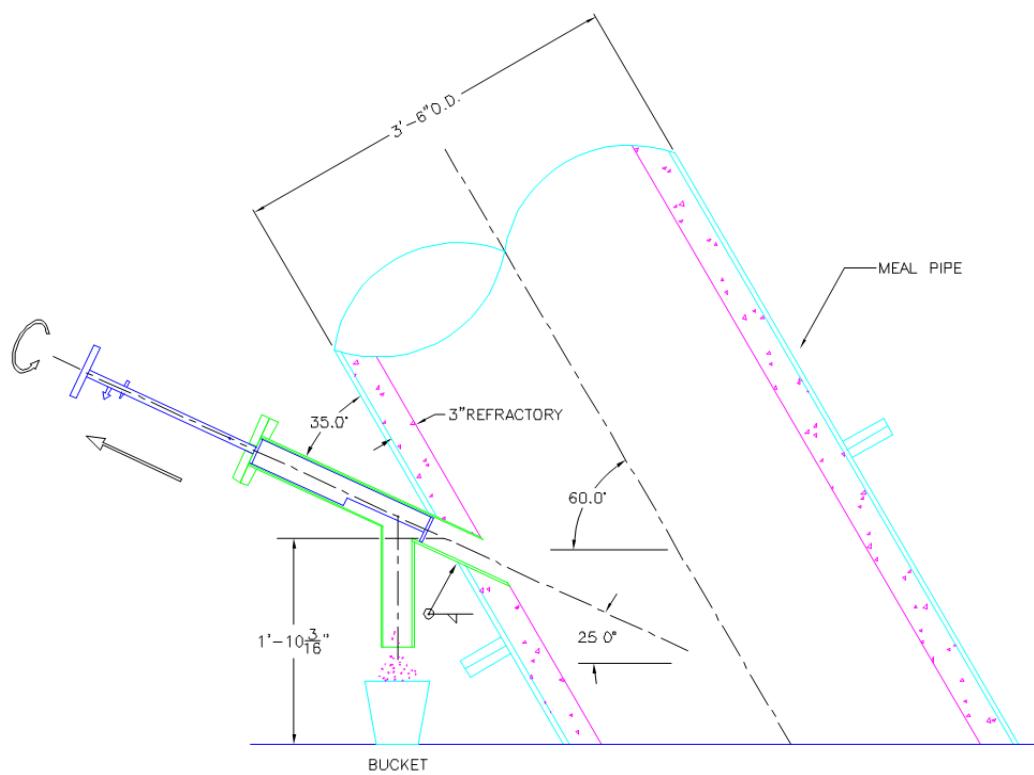
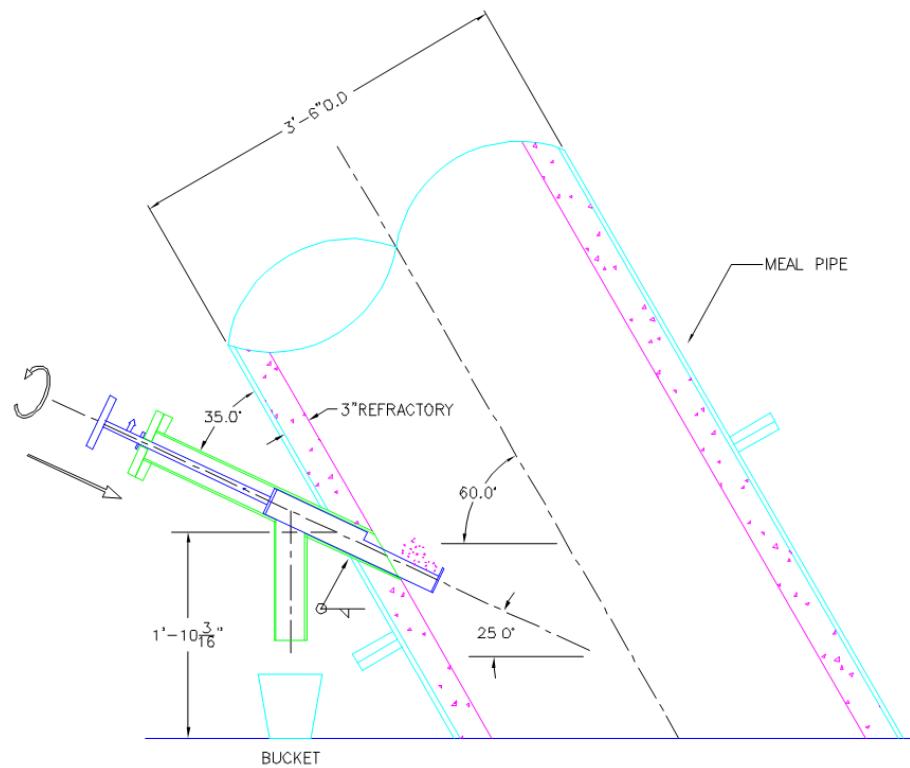
The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

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## Annex 5: Hot meal sampler

(courtesy: Holcim US)



## Annex 6: Method to optimize SO<sub>3</sub> in the cement

(courtesy: Holcim France-Benelux)

The optimization exercise has to be realized on an industrial scale for all different cement types produced. Once the cement mill is in stable conditions, increase deliberately the dosage of calcium sulfate in order to produce cement out of standard for a short period. The cement should be directed to a transition silo or directly "diluted" in the normal silo.

### Notes

- ▶ Foresee to take a clinker sample in order to determined its SO<sub>3</sub> content
- ▶ The Blaine might increase a little bit, but do not touch the grinding system
- ▶ At a certain moment, the cement analysis will detect an elevated SO<sub>3</sub>, for instance 5%, this will be the SO<sub>3</sub> at time zero (t<sub>0</sub>)

### Then

Stop the weigh feeder of Ca sulfate (or reduce the Ca sulfate addition by a factor of 2 or 3 to avoid a too strong effect) and take a sample of 5-10 kg every 5 minutes (quantity depends on type and number of tests to be realized).

SO<sub>3</sub> t<sub>5</sub>  
SO<sub>3</sub> t<sub>10</sub>  
SO<sub>3</sub> t<sub>15</sub>  
SO<sub>3</sub> t<sub>...</sub>

You will observe that the SO<sub>3</sub> of the cement will decrease rapidly. Usually, the exercise is finished within an hour. Once the sample collection is complete, put the Ca sulfate weigh feeder back to the original set point.

Test the samples with different SO<sub>3</sub> for desired properties (e.g. setting time, strength, shrinkage), and establish corresponding curves as a function of the SO<sub>3</sub> content, e.g. strength vs. SO<sub>3</sub> in order to determine the optimum SO<sub>3</sub> content to achieve desired cement performance.

Testing of cement with unusually high or low SO<sub>3</sub> will provide useful information if someday the plant happens to be in this kind of situation.

### Recommendation

Carry out a SO<sub>3</sub> optimization every time there is a change in:

- ▶ composition of clinker (or clinker factor)
- ▶ composition of MIC (or addition%)
- ▶ fineness
- ▶ type of Ca sulphate
- ▶ change in fuel mix

Optimum SO<sub>3</sub> will help to optimize fineness, strength, workability and other cement properties.

**Optimize SO<sub>3</sub> ... it doesn't cost a lot and can provide a great benefit!**

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