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GENERATION OF PETROLEUM COKE IN THE REFINE OF HEAVY OILS AND ITS USE IN ROTARY KILNS OF CLINKER PRODUCTION

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Abstract. *The drop in quality of a portion of the extracted petroleum in the world today is verified due to the decrease of the API gravity, the increase of sulfur content and sludges connected to the fact that the market demand increase for light fractions which represent challenges to be overcomed by the petroleum industry. The coking process is the option adopted by the refining sector for the increase of production of such necessary light derivatives. However, in some cases this process also produces petroleum coke with a low volatile, high sulfur content, and variable hardness depending on the characteristics of the petroleum and on the operational conditions. As the petcoke production is growing, its consumption should follow this tendency. To be used as fuel, the petcoke should be taken to an appropriate particle size for its burning, however its increase in hardness elevates the grinding cost. Besides, the high sulfur content requires appropriate treatment systems to avoid the emission of sulfurous products in values above of that allowed by the environmental legislation. Therefore, this work discusses the generation and the use of petroleum coke as fuel, mainly the high sulfur content one, in the rotary kilns of clinker production of cement factories. It is also analyzes the alkaline environment of the clinker kiln due to the use of the limestone as the main raw material, evaluating the sulfates formation which incorporate to the clinker, minimizing the sulfurous gases emissions to the atmosphere.*

Keywords: *petroleum; petroleum refine; coking; petroleum coke; rotary kilns.*

1. Introduction

The petroleum, a dark viscous liquid and of a distinctive odor, is known from primitive times. It is a multi component mixture formed by hydrocarbons, resins, and asphaltens presenting impurities such as sulfurous compounds, nitrogen and metallic compounds among others (Ellis e Paul, 1998). Since the pioneering work of Drake who in August of 1859, discovered petroleum in a 27 meter deep terrestrial well (Pees, 2004 and IMP, 2004), the oil well drilling technology greatly evoluted from deep water offshore production, to wells more than 5,000 meters deep (Estrella, 2003). Today, petroleum quality extracted in the several parts of the world varies from light from The Middle East, to the extremely heavy ones extracted in China, (Zhao et al, 2004).

2. Characteristics and types of petroleum

An important petroleum characterization index is its density expressed in API gravity (American Petroleum Institute). According to Nelson (1949), the density in API rating is defined by the Eq. (1), in the which - d - represents the relative density at 15.6 ^{o}C (60 ^{o}F). In this manner, the crude oils API gravity is inversely proportional to the relative density. The petroleum, according to the density in API gravity, is classified according to Tab. 1.

$$^{o}\mathrm{API} = \frac{141.5}{\mathrm{d}} - 131.5 \tag{1}$$

Table 1 - Petroleum Classification.

Petroleum	Density (g/cm^3)	API rating
Extra-heavy	>1.0	10.0
Heavy	1.0 - 0.92	10.0 - 22.3
Medium	0.92 - 0.87	22.3 - 31.1
Light	0.87 - 0.83	31.1 - 39
Super-light	< 0.83	> 39

Source: IMP (2004)

The density of petroleum is an important factor in petroleum processing because the refining units are projected according to the greatest or smallest availability of light and heavy products. Therefore, a distillation column projected for light petroleum, was projected to present smaller drainage of products through the bottom and larger drainage of products through the top. To distill heavy petroleum, the distillation column is projected for larger flow at the bottom and smaller flow at the top. When the characteristics of petroleum are changed, problems appear, such as flooding at the bottom of the distillation columns or overflow at the top of these equipments. With the increase of petroleum fields exploration, the petroleum API rating has been decreasing. Since the United States of America imports petroleum from several parts of the world, the results of petroleum researches processed by them, are reasonably significant as world average. Table 2 illustrates this fact.

Table 2 - Variation (%) of the API gravity in the imported and processed petroleum in the USA.

Year	< 20	20.1 a 25.0	26.1 a 30.0	30.1 a 35.0	35.1 a 40.0	40.1 a 45.0	>40
1978	1.26	3.57	7.93	38.79	31.66	13.48	3.31
1982	3.39	14.90	11.72	35.58	23.76	8.44	2.20
1986	5.54	19.36	14.12	27.49	25.74	3.65	4.11
1990	3.64	14.96	18.13	34.44	23.21	2.94	2.67
1994	3.80	18.98	18.46	30.77	23.37	2.75	1.87
1998	5.84	20.29	13.99	35.62	20.81	1.88	1.57
2000	6.21	18.88	13.41	36.90	19.83	3.44	1.35
2001	8.02	20.77	11.62	36.03	19.59	2.74	1.23

Source – EIA (2002).

According to Swain (2002), in the period from 1991 to 1995, the petroleum API density processed in the USA decreased an average of 0.07 API rating per year, while the sulfur content has been increasing at a rate of 0.002% in mass/year, in a clear demonstration of a tendency in quality decrease of the extracted petroleum. The petroleum can present sulfur in free form, or as in combined form. In the combined form, sulfur can appear in the form of hydrogen sulfite, mercaptans, organic sulfites, cyclical and other organic compounds. Other important contaminants are the heavy metals such as Vanadium, Nickel, Copper and Iron (Garcia, 2002).

3. The production process of petroleum coke

3.1. The process history

The history of the process of petroleum coking began in the pioneering refineries of northwestern Pennsylvania in the decade of the 1860's. Those refineries distilled petroleum in a batch operation, using small iron stills to obtain kerosene, very much used in illumination. Heat was supplied by direct fire from wood or burning coal and it ended up coking the petroleum in the bottom of the distiller. The removal of the formed petcoke was made with pickaxes, shovels and wheelbarrows. From 1912 to 1935, the Burton Process developed by Standard Oil in Whiting, in the State of Indiana, converted gas oil into gasoline producing petroleum coke, and drum decoking was done by the unrolling of a long chain left inside the drum before the formation of coke. The development of decoking by hydraulic system happened in the end of the thirties by perforating the coke with high pressure water jets (Ellis e Paul, 1998).

3.2. Processes types

The coking processes have the virtue of residual fraction elimination of heavy oil loads, at the formation cost of a carbonic solid product, producing light derivatives of LPG and gasoline. Presently, there are three petcoke production processes: delayed, fluid-coking and flexi-coking in a fluid bed gasifier (Speight, 2004).

3.2.1. Delayed Coking process

The process happens in a semi-batch operation, in which the load of vacuum residue is heated to about 500 °C, after which it is fed into one of the two coke drums. The reactions happen in the kiln and the coke, with a delay, is formed in the drum. The gaseous result consisting of gases and distilled products exit through the top of the drum at about 435 °C and the coke accumulates in the drum. When the drum is full, the load is diverted to another drum and the coke is removed from the first drum, normally by the use of water under high pressure at about 190 atm. When the second drum is completely full of coke, the operation is diverted to the now empty first drum. A typical cycle takes 48 hours. The coke production yield varies significantly with the fed load composition (vacuum residue), the unit project, and operation. Table 3 shows the coke percentage yield, liquids and gaseous derivatives in function of the API degree vacuum residue, which is the load fed into the coking unit.

Table 3 – Petcoke Percent yields in relation to vacuum residue.

Vacuum Residue (°API)	Coke	Liquids	Gases
Light (10 – 14)	25	68	7
Heavy (6 – 10)	35	58	7

Source – Adams (1994).

3.2.2. Fluid-coking process

The fluid-coking process (Fluidized bed coking) is a continuous process in which the warm vacuum residue is sprinkled at the coke particles fluidized bed. The coking occurs on the surface of these particles at temperatures between 510 and 520 °C. The coking vapor rises to the reactor top where it is abruptly cooled by the contact with medium derivative products or fresh feed. The necessary heat for the cracking reactions is supplied by controll burning part of the coke, to heat up the remaining solids. The fluidized bed temperature and the residence time of the load components in the bed, determine the products yield.

3.2.3. Flexi-coking process with a fluidized bed gasifier

The coking process in fluidized bed with gasification is an alternative process to the fluid-coking process, which uses a coking gasifier to convert the excess coke into a gaseous mixture formed by carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2). In this process, the coke is transformed into a gaseous mixture of low calorific energy in a fluidized bed gasifier using water steam and air. The air is supplied to the gasifier to maintain the temperature between 830 and 1,000 °C, but it is insufficient to burn all the coke.

3.2.4. Comparative composition of petcokes produced in the three processes

The composition of petcokes produced by the mentioned processes is presented in Tab.4, the objective table, only to show the relationship H/C linked to the severity of the process, since the loads are not of the same origin.

Table 4 – Comparative, medium composition between the mentioned petcoke processes.

Composition (Mass %)	Coke production process		
	Delayed	Fluid-coking	Flexi-coking with gasification
Carbon (C)	87.9(1)	86.3	94.9
Hydrogen (H)	3.51(1)	2.2	0.3
H/C	0.47(1)	0.31	0.04
Nitrogen (N)	1.61(1)	2.4	1.1
Sulfur (S)	7.5(1)	6.9	2.8
Oxygen (O)	-	0.9	0
Ashes	0.33(1)	1.3	1.0
Density (g/cm^3)	2.00(2)	0.80	0.96

Source – Adapted from Furimsky (2000), Salvador et al (2003) (1) and Garcia (2002) (2).

4. Types of petroleum coke

The petcoke obtained directly from the production unit is called green coke. The calcined coke is the green coke that was submitted to a calcination process. In this process, the green coke is heated to about 1300 °C in rotary kilns, losing volatile matter and increasing its hardness. The harder the coke, the smaller the HGI (Hardgrove Grindability Index) value measured according to ABNT NBR 8739 (1985). Table 5 shows the composition of green and calcined coke.

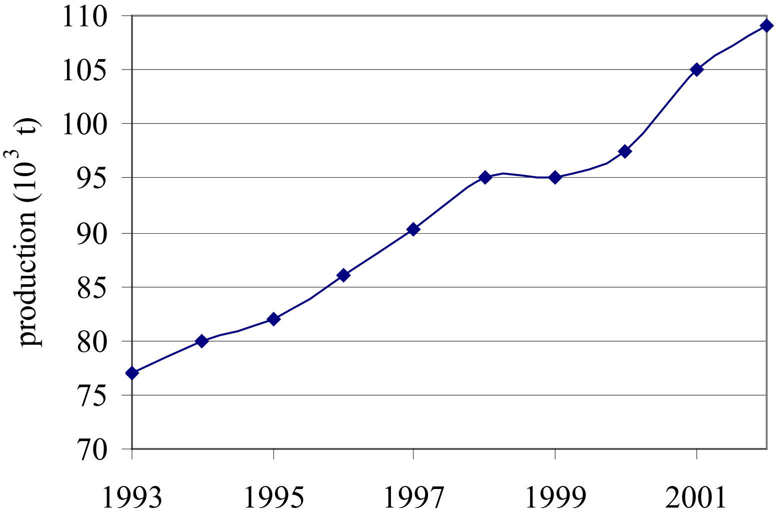
Table 5 - Comparison between the composition of petroleum green coke and calcined coke.

Component	Green coke (% wt) (1)	Calcined (% wt) (3)
Carbon	84 – 97	99
Sulfur	0.5 – 7.5	0.1
Volatile matter	2 – 15	0.4
Hydrogen	Até 5	-
Ashes	0.1 – 0.8	0.5
LCP (kJ/kg)	34,300 – 36,000	-
Hardness HGI	68 – 80 (2)	31 (4)

Sources: CPRH N. 1007 (1); PETROCOQUE (2003) (2); WWI Procat (2002) (3) and Barros et al (2003) (4).

5. Worldwide production of petroleum coke

The worldwide production of petroleum coke reached 81 Mt (million of tons) in 2001, 83 Mt in 2002 and should surpass 88 Mt in 2005. The United States of America is the largest producer, accounting for about 66% of the world production. About 57% of the American production comes from the Gulf of Mexico coast (Texas and Louisiana). In the United States, about 35 refineries produce petroleum coke in appreciable amounts (more than 1000 t/day) (Dynamics, 2004). The petcoke production is growing in the USA refineries due to quality deterioration of crude oils processed. Figure 1 shows the production evolution of this petroleum derivative between 1993 and 2002 (Swain, 2003). It can also be observed that within this period, petcoke production increased by about 40%.



Source – Swain (2003).

Figure 1 – Petcoke evolution production in the USA.

6. The use of petroleum coke as fuel

In principle, any type of petroleum coke can be used as fuel. Although, the green coke from the delayed coking process presents better conditions of burning due to its larger volatile matter content. Besides, it is it that presents larger HGI, in other words, it is the one with the smallest resistance to the grinding operation. The combustible coke can reach up to 100 HGI and 12% of volatile matter (Borges, 2003). According to the Technical Norm CPRH N. 1007, in order to be used as fuel, the green coke must have particles smaller than 1,00 mm, corresponding to a 16 mesh Tyler sieve - USA. According to Ecoinvest (2004), the price difference between the petroleum coke (US\$1.13 for 10^6 BTU) and the fuel oil (US\$2.08 for 10^6 BTU) or the natural gas (US\$2.13 for 10^6 BTU), is attractive. Table 6 shows prices of petroleum coke according to the HGI index and sulfur content.

Table 6 – Prices of petroleum coke according to sulfur content and HGI hardness.

Origin	Sulfur (%)	HGI	Price Range (US$/t)	Trend
U.S. Gulf/ Venezuela	4 – 5	<50	30.00 – 32.00	to increase
	6	35 – 45	22.00 – 25.00	to increase
	6	50 – 70	23.00 – 26.00	to increase
U.S.West Coast	3	45 – 50	43.00 – 45.00	stable
	4	45 – 50	40.00-42.00	stable

Source: Energy Publishing (2004).

The consumer market becomes separated between the ones that consume green coke and the ones that consume calcined coke. The worldwide market profile of green coke use in the year of 1999 is presented in Fig. 2. It is clearly observed in this illustration that the cement production segment is the greatest consumer of petroleum coke. In the year of 1999, petcoke world production was about 48 million tons according to IEA-COAL (2004).

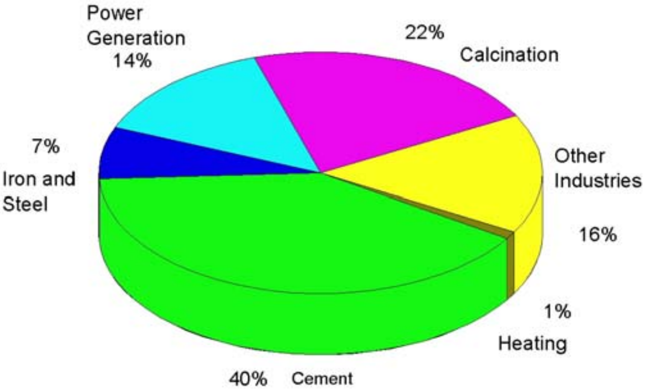


Figure 2 – Green-coke consumer market in 1999 (IEA-COAL, 2004).

7. Cement worldwide production

The worldwide cement production in 2002 was of 1,790 million tons, and in 2003 of 1,870 million tons, representing a growth of 4.5%. Based on the global population growth and on the increase of the world gross domestic product supplied by The United Nations Organization, it is foreseen, for the period between 2003 and 2020, an increase in the cement world consumption in the order of 3.6% according to World Cement (2003).

7.1. Rotary kilns of clinker production

The clinker is the main raw material of the cement. In the rotary kilns, chemical reactions take place which leads to the formation of clinker. The dry process is the most used. The main raw materials are: limestone, clay, sand and iron ore, which supply $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3. The rotary kiln system consists of preheaters (several stages of cyclones), calcinator, rotary kiln, clinker and air ducts cooler for the exaust gases from the kiln combustion system. The raw materials are fed through the top of the pre-heaters tower system. Initially water evaporation contained in the raw occurs. Following, the load is pre-calcinated, beginning the dissociation reactions, generating carbon dioxide (CO_2). In the calcination zone, at temperatures around 850 ^oC, all of the carbonates are decomposed into its respective oxides. The reactions between oxides in the raw materials, called clinkerization reactions, take place in the rotary kiln burning zone at temperatures that reach around 1,500 ^oC. The clinker is cooled in a rapid manner in order to reach temperatures in the range between 100 and 200 ^oC. The cooling air is heated, and it is used as secondary and tertiary air in the kiln combustion system. With the appropriate additions, the ground clinker turns into Portland cement. The exhaustion gases leave the preheater system at temperatures around 330 ^oC, proceeding to the grinding system and the electrostatic precipitator (Cembureau, 1999 and Bauer, 2003).

7.2. Chemical reactions of sulfurous compounds in the rotary kiln system

The sulfurous compounds originated from reactions between the sulfur present in fuels or raw materials with the oxygen from the combustion air can react with calcium, sodium, and potassium compounds contained in the raw materials. Table 7 shows a summary of these chemical reactions (PCA, 2001).

The Periodic Table of Elements classifies calcium and magnesium as earthy alkaline metals; sodium and potassium as alkaline metals. Therefore, the alkaline nature of the rotary kiln system is evidenced by the presence of calcium, magnesium, sodium, and potassium compounds, generating favorable conditions for the retention of sulfur oxides produced by the petcoke burning. The products of these chemical reactions, the sulfates, remain incorporated to the clinker.

Table 7 - Chemical reactions between SO_2 and the rotary kiln load.

Zone of system	Chemical reactions	Equation
Raw material in the precipitator	$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$	(2)
Preheat zone	$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$	(3)
Calcining zone	$CaO + SO_2 \rightarrow CaSO_3$ $CaSO_3 + 0{,}5\ O_2 \rightarrow CaSO_4$	(4) (5)
Burning zone	$Na_2O + SO_2 + 0{,}5\ O_2 \rightarrow Na_2SO_4$ $K_2O + SO_2 + 0{,}5\ O_2 \rightarrow K_2SO_4$ $CaO + SO_2 + 0{,}5\ O_2 \rightarrow CaSO_4$	(6) (7) (8)

Source – PCA (2001).

7.3. Sulfur Dioxide (SO_2) Absorption

Sulfur dioxide (SO_2) emissions are nearly independent of the sulfur input by the fuel. It seems to be closely correleted exclusively to the amount of sulfides in the raw materials, because the sulfide oxidation form SO_2 at temperatures between 400 – 600 °C, in the cyclone Stage II. In the calciner, due to the calcination of $CaCO_3$, great amount of free CaO exists in the temperatures that favor the dessulfurization reactions that take to the $CaSO_4$ formation. The SO_2 produced in the burning zone can be combined with free CaO and also with alkalis (PCA, 2001). It is necessary to calculate the Gibbs free energy of the reactions presented in Table 7, to verify her behavior, because a chemical reaction only happens when its Gibbs free energy has a negative value (Smith and Van Ness, 1987).

The Gibbs free energy for a chemical reaction, according to Smith and Van Ness (1987) is defined by Eq. (9). The Eq. (10) and (11) calculate each one of the terms of Eq. (9).

$$\Delta G^o = \Delta G_P - \Delta G_R \tag{9}$$

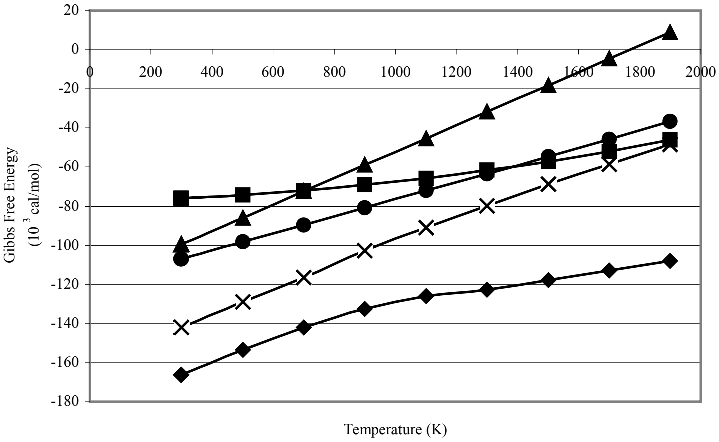
$$\Delta G_P - \Delta G_R = \sum n_{Pi}[(h - h_0) - T.(s - s_0)]_{Pi} - \sum n_{Ri}[(h - h_0) - T.(s - s_0)]_{Ri} \tag{10}$$

$$\sum n_k[(h - h_0) - T.(s - s_0)]_k = \sum n_k[\int_{T_0}^{T} Cp_k.dT - T.(\int_{T_0}^{T} Cp_k.\frac{dT}{T})] \tag{11}$$

Where, ΔG_P e ΔG_R represent the variation of Gibbs free energy of products and reagents, respectively, **n** the number of mol involved in the chemical reaction, **h** and **s** the specifc enthalpy and entropy, h_0 and s_0 the formation enthalpy and entropy and **Cp** the heat capacity for each substance. The relative values to the calculation of the heat capacity for each substance were obtained from Carvalho et al (1977) and Perry (1999). The Gibbs free energy values for the SO_2 absorption reactions in the rotary kiln system, calculated by Eq. (9), are presented in Fig 3.

From Fig. 3, it can be observed that partial absorption chemical reactions of SO_2 happen in the rotary kiln system, where the maximum temperature of solids is about 1,450 °C (1,723 K). The remaining to reach levels that can arrive to 95 % happens in the precalciner. In the rotary kiln burning zone, SO_2 and the alkaline and calcium sulfates are the stablest forms, and the generated sulfates are incorporated to the clinker. The calcination zone presents great conditions for the SO_2 capture, by the free CaO. The grinding in line of the raw materials, although done at a low temperature, is an efficient SO_2 absorber due to the presence of $CaCO_3$ finely divided.

The potassium sulfate (K_2SO_4) presents ebullition point at 1,689 °C, favoring his passage for the kiln, in the solid state. Already the calcium sulfate $CaSO_4$ presents melt point around 1,400 °C (Chahine, apud Silva, 1994). Thus $CaSO_4$ tends to dissociate, in temperatures above 1,650 °C, according to Fig. (3), regenerating the CaO and SO_2.



-■- $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$; -●- $CaO + SO_2 \rightarrow CaSO_3$; –x- $Na_2O + SO_2 + 0{,}5\ O_2 \rightarrow Na_2SO_4$;
-◆- $K_2O + SO_2 + 0{,}5\ O_2 \rightarrow K_2SO_4$;) -▲- $CaO + SO_2 + 0{,}5\ O_2 \rightarrow CaSO_4$.

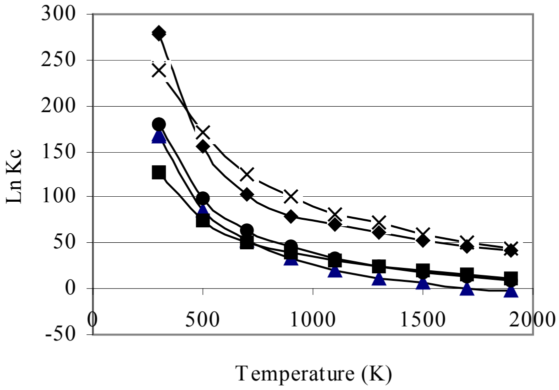
Figure 3 - Values of Gibbs Free Energy for the chemical reactions of SO_2 absorption in the rotary kiln system.

The equilibrium constant that relates the concentrations of the products in relation to the concentrations of reagents, is calculated by Eq. (12), according to Smith and Van Ness (1987).

$$K = \exp(-\frac{\Delta G^0}{R.T}) \tag{12}$$

Where R is the universal constant for gases and T is the absolute temperature for the ΔG^0 value.

The values calculated for equilibrium constants obtained by Eq. (12) for chemical reactions of SO_2 absorption are in Fig. 4.



-■- $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$; -●- $CaO + SO_2 \rightarrow CaSO_3$; –x- $Na_2O + SO_2 + 0{,}5\ O_2 \rightarrow Na_2SO_4$;
-◆- $K_2O + SO_2 + 0{,}5\ O_2 \rightarrow K_2SO_4$; -▲- $CaO + SO_2 + 0{,}5\ O_2 \rightarrow CaSO_4$.

Figure 4 –Values of equilibrium constants for SO2 absorption chemical reactions in the rotary kiln system

Fig. 4 shows that, as the temperature rises, that is, as the raw materials and their products flows in the direction of the rotary kiln burning zone, the value of the equilibrium constant decreases, showing that it reduces the capacity of SO_2 absorption, even though this absorption continues to happen. Therefore, in the precalciner the absorption levels are larger than in the rotary kiln.

Such fact explains the best capacity of the rotary kiln with preheater and precalciner can use petcoke with high sulfur content, because in the calciner and in the kiln it exists great amount of free CaO, presenting thermodynamic conditions for SO_2 absorption with alkaline and calcium sulfates formation (Silva, 1994).

8. Conclusion

The crude oils are becoming more and more heavy, producing less lighter derivatives and much heavier ones. The light fractions consumption is increasing, requiring coking units at petroleum processing plants. Therefore, petcoke production is increasing, calling for the opening of the consumer market. Nevertheless, the high content of sulfur limits the use of petcoke as fuel, in several process, because of the necessity of treatment of exhaust gas to conform to the environmental legislation.

The Portland cement production process contains raw materials in which its alkaline and alkaline earthy products are capable to chemically react with the SO_2 generated in the combustion, removing it from the gaseous currents and producing sulfates that are incorporated to the clinker, therefore minimizing the emission of gaseous pollutants.

In this manner, the cement industry potentially presents itself as a great consumer of petroleum coke due to the thermodynamic characteristics of the rotary kiln system, favorable to the absorption of SO_2.

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10. Term of responsibility

The authors are solely responsible for the information contained in this article.