

THE SO_x GENERATION FOR THE HIGH SULFUR CONTENT PETROLEUM COKE COMBUSTION IN ROTARY KILNS OF CEMENT CLINKER PRODUCTION.

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Abstract. *The petcoke world production in the refineries is increasing due to the following factors: crescent heavy oils offer; fuel oil substitution in the industrial use for other energy ones, mainly the natural gas; and the need to produce more light fractions, also produced in the coking process. The petcoke concentrates the petroleum heaviest pollutants, among them the sulfur. In this petcoke combustion there is the SO_x formation, demanding the exhausted gases treatment for subjects of Environmental Legislation. In the cement kilns industry the sulfur can be introduced so much through the fuels, as well as, through the raw materials. This work presents an analysis of the petroleum coke use as fuel in the cement industry. It is discussed the SO_x generation and its absorption in the clinker production process, where the combustion happens in alkaline environment. The maintenance of an oxidizer atmosphere in the kiln is a fundamental factor for the SO_x absorption, seeking to impede the formed sulfates dissolution. The work concludes showing that the rotary kiln of clinker production is a system capable to absorb SO_x that will be incorporate to the clinker, the final product, without quality loss.*

Keywords: *heavy oils, petcoke, Portland cement, combustion, SO_x.*

1. PETROLEUM

The petroleum is a multicomponent mixture, formed predominantly by hydrocarbons. The crude oils are classified according to his API gravity, according to the Tab. 1.

Table 1 – Crude oils classification.

Crude oil	Density (g/cm ³)	API gravity
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) e Petrobras/Glossário (2005).

Another classification consists on considering the crude oils as conventional and unconventional ones (USGS, 2003). The conventional oils present minimum 22 API gravity and viscosity, to the temperature of the reservoir, of 100 cP (centipoise), according to USGS (2003). According to Mandil (2002) the unconventional oils are all the raw ones with API gravity below 20. The heavy oils have API gravity between 10 and 20. The extra heavy oils and bitumen have API gravity below 10 and the difference among them is in the respective viscosities to the temperature of the reservoir: larger than 10.000 cP for the bitumen and smaller than 10.000 cP for the extra heavy oils.

The variation of API gravity of the crude oils processed by the United States of America refineries, in the period from 1998 to 2006, presents the following behavior: the crude oils with API gravity smaller than 20 (heavy crudes) increased its participation of about 5.5% for almost 13%, maintaining the crescent profile along the whole considered period; the crude oils with API gravity between 30.1 and 35 (light crudes) reduced its participation of about 35.5% for about 28.5%, maintaining in the period, a clearly decreasing tendency and the crude oils with API gravity larger than 45.1 (superlight crudes) in the considered period presented a discreet growing profile, going from 1.5% for about 2.5% (EIA, 2007).

According to EIA (2002), from 1980 to 2002, the sulfur content of the crude oils processed in the USA increased about 56%, growing from 0.9 to 1.4%.

As the USA process crude oils from the most several world producers, it is ended that the crude oils, presented at the international market, are being heavier and with larger sulfur content.

2. PETROLEUM COKE

Petroleum coke is the only derived solid of the petroleum. The coking processes have the virtue of elimination of the residual fraction of heavy petroleum feedstocks, aiming the generation of light fractions of the strip of the gasoline and diesel, at the cost of formation of a carbonic solid product. The petcoke yield in the given coking process tends to be proportional to the feedstock carbon residue content.

The petcoke production, in the period from 1993 to 2002 has been growing in the USA refineries due to deterioration of the processed crude oils quality (Swain, 2003).

Due to the consumption of the petroleum growth with high sulfur content, because of the falling offer of crude oils with low sulfur content, the medium content of sulfur in the petcoke has been increasing. Most of the world petroleum coke production presents sulfur content varying from 2% to 8% and only a small part of that production presents sulfur content below 2%, being difficult to find petcoke with less than 1% of sulfur (Dobel et al, 2006). According to Salvador et al (2003) the properties of some petroleum cokes are presented in the Tab. 2.

Table 2 – Properties of some petroleum cokes.

Component	Sample 1 % (weight)	Sample 2 % (weight)	Sample 3 % (weight)	Sample 4 % (weight)	Sample 5 % (weight)
C	88.5	87.9	88.4	85.8	89.4
H	1.94	3.51	3.70	3.50	3.60
S	6.00	7.47	6.16	5.85	4.02
N	1.63	1.61	1.56	1.70	1.88
Ashes	0.5	0.33	0.12	3.35	0.47
Volatile matter (% dry)	5.17	10.48	10.96	11.09	10.14

Source: Salvador et al (2003).

According to Pulido and Fernández (2007), the petcoke originated from Mexican crude oils presents about 5.7% of sulfur and the petcoke produced from Alberta bitumen, in Canada, presents about 6.8% of sulfur.

2.1. Types of petroleum coke

Nowadays, there are three processes of petcoke production: delayed coking, fluidized bed flexi coking and fluidized bed flexi coking with gasification (Speight, 2004). The Brazilian refineries operate with the delayed coking process.

The petcoke obtained directly from the production unit is called green coke. The calcined coke is a product of processing in another industrial unit, called Green Coke Calcination Unit. An important petcoke characteristic is the grindability degree, defined by Hardgrove Grindability Index (HGI) and the larger the HGI, the easier is the grindability. The volatile matter, another important property, always decreases after its calcination, increasing the difficulty in that petcoke burns.

In beginning, any type of petcoke can be used as fuel, although the petroleum coke needs high temperature for its combustion (Dobel et al, 2006).

The green coke of the delayed coking is the one which presents better burning conditions thought, due to its larger content of volatile matter and larger relationship HC and larger HGI; the combustible coke can reach up to 100 HGI and 12% of volatile matter (Borges, 2003).

2.2. The price of petroleum coke

Due to the high costs in energy, the petcoke shows up as a good option. That option will become more attractive if the process absorbs the pollutants which are generated by the petcoke burns, minimizing the cost of treatment of the exhausted gases (Maning et al, 2003).

The Fig. 1 presents the petcoke cost evolution in function of the cost of the natural gas and the synthetic gas produced by the petroleum coke gasification (GCPA, 2005).

The Fig. 1 also shows that, in the interval from 1995 to 2004 the price of the petcoke remained practically stable, always below US\$ 1/million of BTU, the synthetic gas produced by the petcoke gasification also presented a stable profile, around US\$ 3/million of BTU while the natural gas, from 1995 to 1999, presented its price below synthetic gas one and, starting from 1999, a growing price profile has been presented a little more than US\$ 6/million of BTU in 2004.

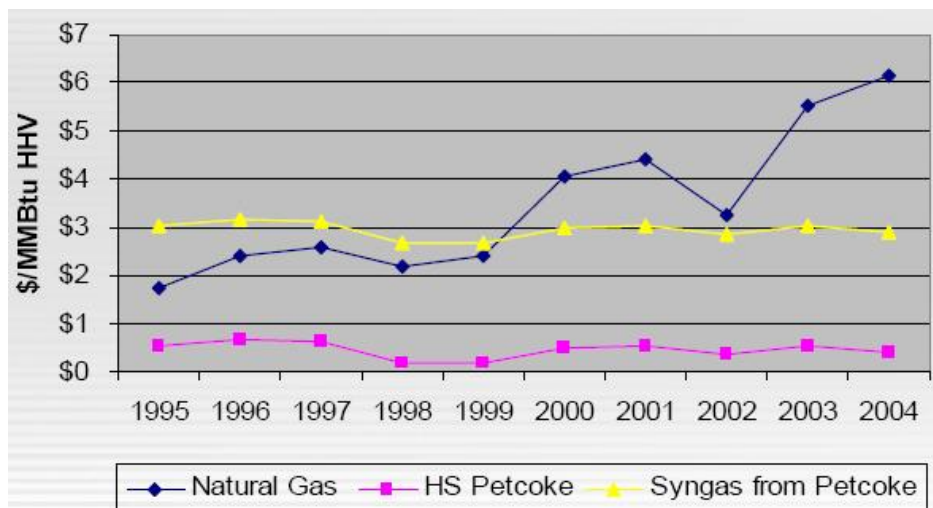


Figure 1 – Cost of the petcoke compared with the natural and synthetic gases.
 Source: GCPA (2005).

The Tab. 3 displays a comparison of prices (relative to 2007) among the petcoke produced in the USA Gulf area and the produced ones in Venezuela. It's noticed that the sulfur content interferes more in the prices than the HGI. Except for the petcoke with HGI <50 and sulfur among 4 - 5% and the petcoke with 45 <HGI <50 and sulfur in 3% (U.S. West), the other petcoke ones present a price elevation tendency.

Table 3 - Petcoke prices in function of sulfur content and hardness HGI.

Origin	Sulfur (%)	HGI	Price (US\$/t)	Trend
U.S. Gulf/ Venezuela	4 – 5	<50	60.00 a 65.00	Stable
	6	35 a 45	50.00 a 52.00	To grow
	6	50 a 70	53.00 a 56.00	To grow
U.S. West	3	45 a 50	60.00 a 63.00	Stable
	4+	45 a 50	57.00 a 61.00	To grow

Source: Energy Publishing (2007).

2.3. Petcoke world production

The petcoke world production reached 81 Mt (million of ton) in 2001, 83 Mt in 2002 and it was foreseen to cross 88 Mt in 2005. The USA are its largest producer, answering for about 66% of the world production. About 57% of the American production comes from the coast of the Gulf of Mexico (Texas and Louisiana). In the United States, about 35 refineries produce petroleum coke in appreciable amounts (more than 1000 t/d). The Tab. 4 shows the world production of petcoke, in percentage (Dynamics, 2004).

Table 4 – Petcoke world production.

Producing Areas	Participation (%)
North America	69.5
South America	9.1
Europe	8.5
Asia	6.9
Former-USSR	5.0
Africa	0.5
Oceania	0,5

Source: Dinamics (2004)

3. PRODUCTION OF PORTLAND CEMENT CLINKER

The usual raw materials for the clinker production are the limestone, the clay, the sand and the iron ore, whose medium composition is presented in the Tab. 5, according to PCA (2001).

Table 5 - Raw composition for the clinker production.

Component	% (weight)
CaCO ₃	78.11
SiO ₂	14.67
Al ₂ O ₃	2.53
Fe ₂ O ₃	2.72
MgCO ₃	1.01
SO ₃	0.79
K ₂ O	0.16
Na ₂ O	0.09
H ₂ O	0.23

Source: PCA (2001).

The main contents of the rotary kiln system are the pre-heaters, the calciner and the rotary kiln. It is in that system that the components of the raw materials react amongst each other and with the coming gases of the fuel burns as well, forming the clinker, the main raw material of the cement.

The pre-heaters are of the cyclone type, which change heat among the material fluxes against current; the calcinator is also the cyclone type and it receives the secondary fuel and the tertiary air for the combustion; the rotary kiln is a great load chemical reactor, in a cylindrical one, with rotative movement, slightly inclined, having in its lowest extremity the entrance of the hot gases, which are generated in the burns of the primary fuel and, in the highest extremity, the entrance of the raw materials and exit of the combustion gases. The generating chemical reactions of the clinker occur in the rotary kiln, whose maximum temperature is about 1500 °C, a flame temperature of about 2000 °C (Cembureau, 1999).

3.1. Generation and absorption of SO_x in the rotary kiln system

The entrance of the sulfur and its derived products, in the rotary kiln system, it occurs through the raw materials, when they contain pyrite (FeS₂) and the fuel also (PCA, 2001). The Tab. 6 relates the components of the rotary kiln system of the rotary kiln with the temperatures and the chemical reactions of formation and absorption of SO₂ and SO₃ (PCA, 2001; Zivkovic and Milosavljevic, 1990 and Manovic et al, 2006).

Table 6 - Formation and absorption of SO_x in the rotary kiln system.

Equipment	SO ₂ Generation	SO ₂ Absorption
Pre-heater (100 – 550 °C)	2FeS ₂ + 6O ₂ → Fe ₂ O ₃ + 3SO ₂ + SO ₂	CaCO ₃ + SO ₃ → CaSO ₄ + CO ₂ CaCO ₃ + SO ₂ → CaSO ₃ + CO ₂
Calciner (800 – 850 °C)	Secondary fuel → SO ₂	SO ₂ + CaO → CaSO ₃ SO ₂ + CaO + 0,5O ₂ → CaSO ₄
Rotary kiln (1200 – 1500 °C)	Primary fuel → SO ₂ CaSO ₄ + CO → CaO + SO ₂ + CO ₂	SO ₂ + Na ₂ O + 0,5O ₂ → Na ₂ SO ₄ SO ₂ + K ₂ O + 0,5O ₂ → K ₂ SO ₄ SO ₂ + CaO + 0,5O ₂ → CaSO ₄

Source: PCA (2001); Zivkovic and Milosavljevic (1990) and Manovic et al (2006).

3.1.1. Free energy of Gibbs

A chemical reaction only occurs when its free energy of Gibbs presents negative value (Smith et al, 2000). So, to confirm the occurrence of the chemical reactions presented in the Table 6, it will be calculated the values of the free energy of Gibbs from each one of these reactions.

According to Smith et al (2000), the free energy of Gibbs is defined by the Eq.(1).

$$\Delta G_P - \Delta G_R = \sum n_{Pi} [(h - h_0) - T.(s - s_0)]_{Pi} - \sum n_{Ri} [(h - h_0) - T.(s - s_0)]_{Ri} \quad (1)$$

being ΔG_P and ΔG_R the variation of free energy of Gibbs of the products and the reactants, respectively. The coefficients used to calculate the enthalpy (Δh) and entropy (Δs) variation were obtained by Perry (1999) and by Carvalho et al (1977).

The Fig. 2 presents the calculated values of the free energy of Gibbs of the absorption equations displayed in the Tab. 6; be notice that those reactions are spontaneous in the temperature strip mentioned in the referred table.

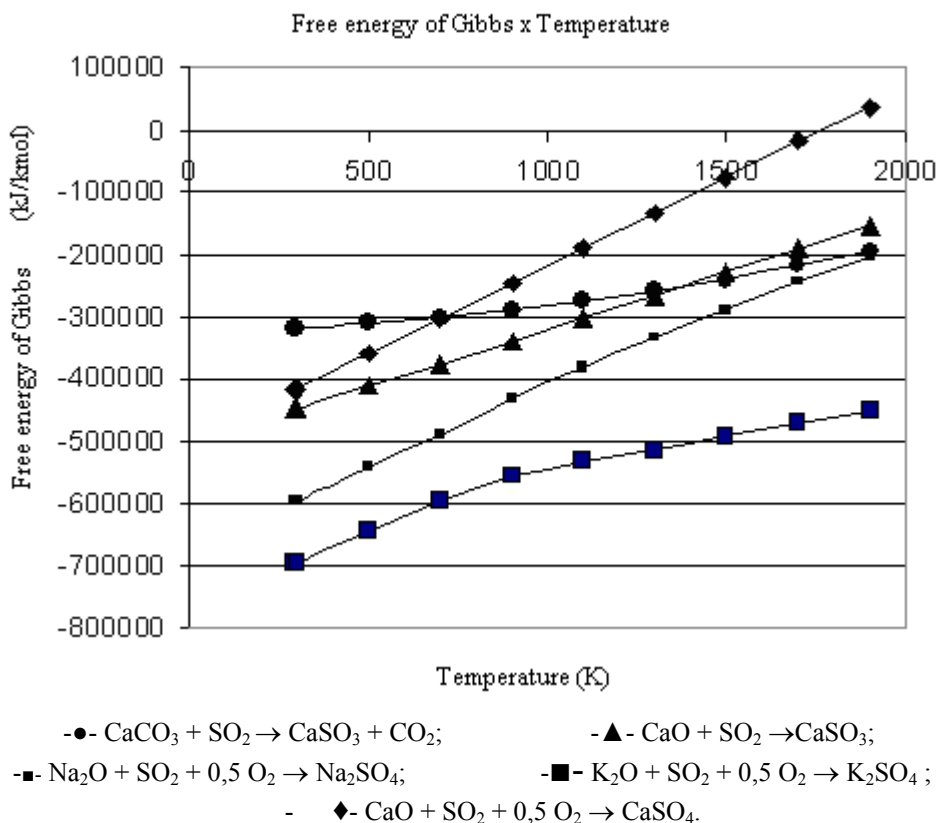


Figure 2 - Free energy of Gibbs values for the chemical reactions of absorption of SO₂ in the rotary kiln.

3.1.2. Equilibrium constant

The chemical reactions are reversible and there will be concentration, pressure and temperature conditions in which reactants and products coexist in an equilibrium state. The main characteristic of the equilibrium state is the fact of being dynamic, it means that is a permanent situation, maintained by the equality of speed of two opposed chemical reactions (Mahan and Myers, 2000).

The equilibrium constant is calculated by the Eq. (2), according Smith et al (2000).

$$K = \exp\left(\frac{-\Delta G}{R.T}\right) \quad (2)$$

In the Eq. (2), ΔG (kJ/kmol) represents the free energy of Gibbs for the chemical reaction, R (kJ/kmol.K) is the gases universal constant and T (K) is the absolute temperature.

The Fig. 3 presents the calculated values of the equilibrium constants of the chemical reactions of the SO₂ absorption in the rotary kiln system.

Although the equilibrium constants indicate a high progress degree or a high conversion, this doesn't mean that a total conversion of the reactants occurs. Through the chemical kinetics, it's possible to estimate the necessary time for the occurrence of such reactions inside the rotary kiln, or pre-heater or calciner.

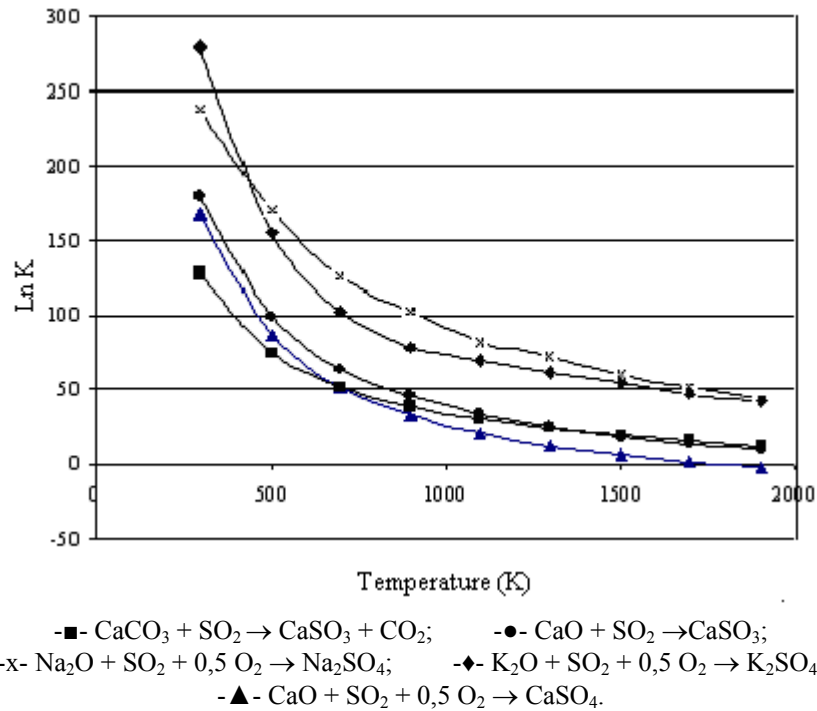


Figure 3 – Equilibrium constants values of chemical reactions of SO₂ absorption in the rotary kiln system.

3.1.3. Chemical reaction residence time

The residence time for a chemical reaction complementation represents the necessary time for the concentration decreasing of a reactant.

The reactions of sulfur dioxide (SO₂) absorption can be considered as the first order ones, according to Hu et al (2006) and the residence time can be calculated by the Eq. (3) (Silva, 1999), being C_{A0} (initial concentration of SO₂), C_A (instantaneous concentration of SO₂), A the pre-exponential factor (1/s), E_a the activation energy (kJ/kmol), R the gases universal constant (8.314 kJ/kmol.K) and T the considered temperature (K).

$$t = \exp \left\{ \ln \left[-\frac{1}{A} \left(\ln \frac{C_A}{C_{A0}} \right) \right] + \frac{E_a}{R.T} \right\} \quad (3)$$

4. MATERIALS AND METHODS

At the Tab. 5 it is observed that in the rotary kiln system if it's analysed quantitatively, the presence of CaCO₃ is more significant than the presence of the other compounds, which are susceptible to react with the sulfur dioxide. Besides that, according to Manovic et al (2006), to considering the presence of Na₂O and K₂O would implicate in a complex model usage and extensive experimental investigation. Thus, in the adopted modeling, it will only be considered to end up the absorption of SO_x the equations that involve the calcium oxide (CaO) in the rotary kiln, the calciner and the calcium carbonate (CaCO₃) in the pre heater as well.

4.1. Application of the modeling for absorption of SO_x

Among several processes and existent configurations of clinker production, the process will be adopted by dry way and the adopted configuration will be the rotary kiln with calciner and pre-heater with four stages, producing clinker under the required specifications (Silva et al, 1993), that is the process wich presents specific consumption of heating (CEC) around 3100 kJ/kg clinker, according to Cembureau (1999). The Fig. 4 shows the rotary kiln system components, presenting the electrostatic precipitator and the in line raw material mill (PCA, 2003).

It will be also considered, that the fuel is the petroleum coke, according to the Tab. 2 and the raw material presents the suitable composition in the Tab. 5.

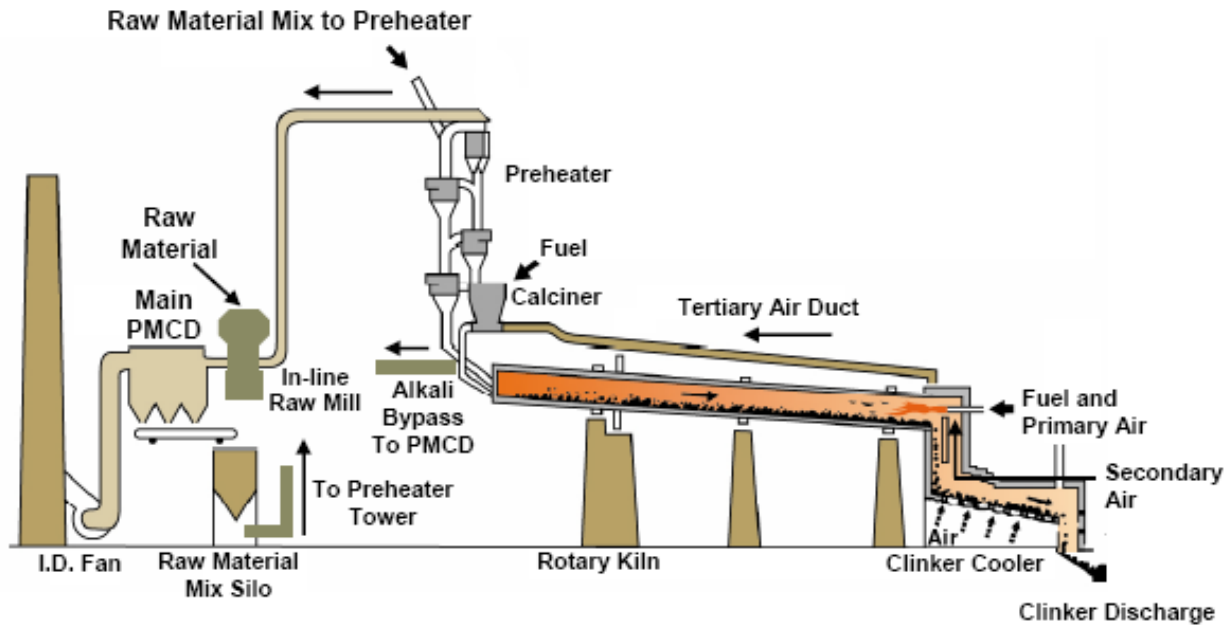


Figure 4 - Schematic view of a rotary kiln system (PCA, 2003).

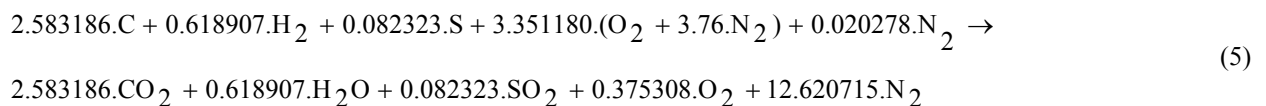
4.1.1. Calculation of the petroleum coke amount and generated SO₂

Then, the petcoke consumption (CP) for clinker kilogram (CLQ) will be calculated by the Eq. (4), where the value of LHV (Lower Heat Value) is 35,162 kJ/kg.

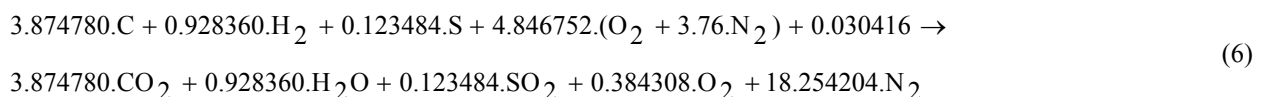
$$m(\text{CP}) = \frac{\text{CEC}}{\text{LHV}} \quad (4)$$

At the Eq. (4) it is obtained the value of 88.2 kg CP/t CLQ; the petcoke combustion takes place as the following way: about 60% of the petroleum coke used in the process is burned in the calciner (secondary fuel) and the remaining 40% form the primary fuel, feeding the main blowpipe, according to AWMA (2006).

The Eq. (5) presents the result of the combustion stoichiometric calculation for the primary fuel, considering free O₂ in the exhausted gases valued in 2.4% in dry base, according to the operational practice of the rotary kiln.



The Eq. (6) presents the result of the stoichiometric calculation of the combustion equation for the secondary fuel, considering free O₂ in the exhausted gases valued in 1.7% in dry base, according to the usual practice in the rotary kiln operation.



4.1.2. Calculation of the raw material amount and the generated SO₂

The Mass Conservation Principle is applied in order to end up the solids mass balance in the rotary kiln system, obtaining the Eq. (7), that calculates the amount of raw m(CRU) in function of the participation of each component of the raw material and so does the petcoke.

$$m(\text{CRU}) = \frac{(1 - p_4.p_5)}{(1 - p_1 - 0.44.p_2 - 0.523.p_3)} \quad (7)$$

being p1 the water in the raw material (%), p2 the calcium carbonate in the raw material (%), p3 the magnesium carbonate in the raw material (%), p4 the ash in the petcoke (%) and p5 the relationship between petcoke and clinker (%). Obtained the m(CRU) value, the values of the components of the raw material are calculated.

The quantification of the production and absorption of SO_x is made through the stoichiometric calculation and the residence time of the involved chemical reactions, the permanence time of the reactants and each part of the rotary kiln system as well.

According to Rebers and Landreth (1997) in the rotary kiln, the gases permanence time is from 4 to 12 s and the 8 s medium value was adopted. In the calciner, the gases permanence time is around 4.6 s, according to Taylor (1997). According to Lee and Lin (2000), the gases residence time in the four stage pre heaters is around 5.5 s. Along with those values, the absorbed amounts of SO₂ will be calculated, considering the proportional absorption to the time of permanence of the gases in each section of the rotary kil system.

The application of the equation for the reaction between the CaO and SO₂, as it was presented in the Table 6 and to the medium temperature of the same table, with the adopted times and the values of the kinetic parameters presented by Ávila (2005), it generates the values presented in the Tab. 7.

Table 7 - Necessary time to the accomplishment of the absorption of SO₂ in the rotary kiln system.

Rotary kiln system place	T (K)	Concentration Initial (kmol/volume)	Time (s)	Concentration Final (kmol/volume)
Rotary kiln	1,448	0.082323	8.0	0.000874
Calciner	1,123	0.124358	4.6	0.011876

Calculating the necessary time to pre heater SO_x absorption as the chemical equations presented in the Tab. 6 and considering that the values of the kinetic parameters, for this absorption, were not found in the researched literature, a calculation procedure was adopted, based on the sulfur mass balance presented by Holaipe and al (1998), producing the values which are presented in the Tab. 8, evidencing that the presence of pyrite is unwanted in the raw materials, do its total oxidation occurs in the pre-heater (Zivikovic et Milosavljevic, 1990). Minimizing the effect provoked by the pyrite presence in the raw material, an alternative is the usage of calcium oxide to absorb SO_x, as chemical reaction presented in the Tab. 6 and it has favorable reaction thermodynamic conditions for its complementation.

Table 8 - Absorption yield (%) in the components of the rotary kiln system.

Equipment	Absorption (%)
Rotary kiln	98.9
Calciner	90.5
Pre-heater	36.7

The operation of the raw materials mill, in line with the exhausted hot gases and positioned after the pre-heater, as it was presented in the Fig. 4, reduces the SO₂ concentration in the strip from 40 to 60%, due to the presence of calcium carbonate particles (CaCO₃) finely divided, propitiating great reaction conditions to SO₂ absorption. When it operates, the mill contributes to the global increasing of the SO₂ tax absorption; however, unlike the rotary kiln that operates continually, the mill only operates the enough time to supply the raw material with size of appropriate particle to the process, it's not an equipment of pollution control in facing to its great electric power consumption (PCA, 2003).

4.1.3. Calcium sulfate (CaSO₄) decomposition through carbon monoxide (CO) in the rotary kiln

The CaSO₄ decomposition might occur inside the rotary kiln if there is the occurrence of the atmosphere reduction. The atmosphere reduction occurs when the concentration of free oxygen in the combustion gases is in such a low value that the carbon monoxide content prevails in relation to the free oxygen (PCA, 2001).

So, It is like this that for levels of oxygen valuing 2.5% the carbon monoxide content is 500 ppm; but to 1.4% of oxygen, the carbon monoxide concentration arises to 2,500 ppm.

The decomposition of the calcium sulfate for the carbon monoxide happens according to the Eq. (8), for values starting from 2000 ppm of CO (Manovic et al, 2006).



As it is observed in the Eq. (8), in a reduced atmosphere, the absorption of sulfur dioxide is prejudiced, because instead of assimilating SO₂ it is liberated by the decomposition of CaSO₄.

The free energy of Gibbs, of the suitable the chemical reaction indicated in the Eq. (8), was calculated by the Eq. (1) and the obtained values are presented in the Fig. 5.

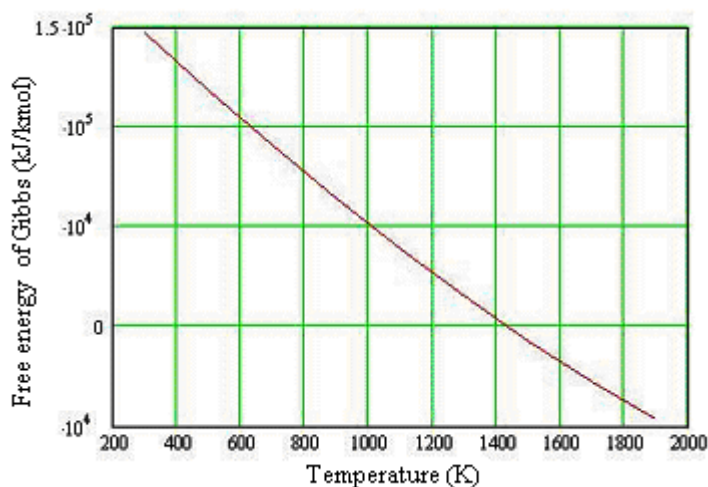


Figure 5 - Free energy of Gibbs variation for the Equation 8.

The Tab. 6 shows that the calcium sulfate is present in all the components of the rotary kiln system. Although, as it can be seen in the Fig. 5, the free energy of Gibbs for the chemical reaction presented in the Eq. 8 only if it turns to be negative for temperatures values a little above 1400 K (1127 °C). Thus, the reaction between CO and CaSO₄ only turns to be spontaneous inside the rotary kiln. In order to minimize this decomposed effect, the combustion develops with excess of air, so that the exhausted gases have oxidizer characteristic, containing, at least, 2.5% of free oxygen impeding, so, the decomposition of the calcium sulfate.

5. CONCLUSION

The petcoke production increase is not an option of the refiners, but a consequence of the petroleum density increase and the necessity of the heavy fractions cracking for the light fractions generation. Due to the elevation of the sulfur content of the different origins processed oils, the tendency is that most of the coke production presents sulfur content that can reach values up to 8%. The high sulfur content in the petcoke restricts its usage to the processes, capable to absorb the sulfur oxides (SO_x) generated in the combustion, without any need of a subsequent treatment of the exhausted gases, minimizing, like this, the operational costs, as it's the case of the systems which use fluidized bed and rotary kiln of clinker production. The system of the rotary kiln presents in all of its components, favorable thermodynamics conditions to the SO_x absorption. The pyrite presence in the raw material generates SO_x that is liberated at the first stage of the pre-heater, whose yield of SO_x absorption is low. Thus, due to the pyrite content in the raw material, the petcoke might be used with larger or smaller sulfur content. In order to avoid the decomposition of the formed calcium sulfate, liberating SO_x, a constant monitoring is necessary so that, the conditions of the petcoke combustion occur, always in an oxidative atmosphere. With the monitoring of the pyrite content in the raw material as well as the variables of combustion, the cement industry has presented itself as an ideal petcoke consumer.

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