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RELATIONSHIP BETWEEN THE SULFUR CONTENT IN PETCOKE AND PYRITE ON THE PROCESS OF CLINKER CEMENT PRODUCTION.

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Abstract. *The rotary kiln system of Portland clinker cement production presents favorable thermodynamics conditions for the absorption of sulfur dioxide****, that´s why*** *the cement industry* ***is*** *an ideal consumer of petcoke of high sulfur content as fuel.****Although*** *the pyrite presence in the raw materials liberates SO_2 in the preheater****, that is*** *the component of the system with smaller capacity of absorption of that sulfur compound.* ***Thus,due to*** *the pyrite content in the raw materials, the selection of the type of petcoke to be used* ***should be made*** *. The analysis* ***must*** *be accomplished* ***since*** *operational information of the process of cement clinker Portland production, stoichiometric calculations, free energy of Gibbs, balance and kinetics of the chemical reactions of SO_2 absorption in the system of the rotary kiln of clinker production. This work has* ***as its main*** *objective to show the relationship among the petcoke with the raw materials through an equation deduced theoretically.* ***Therefore, the compositions of petcoke and raw materials were used as*** *outline conditions, considering the percentile proportion among the amounts of petcoke as primary and secondary fuel. They* ***also*** *integrate* ***to*** *the outline conditions, the yield of the SO_2 absorption, in the rotary kiln and in the calcinator; the yield of the SO_2 absorption in the preheater was deduced* ***of literature data*** *of the sulfur balance of an existent plant.*

Keywords*: cement industry, pyrite, petcoke, SO_2 absorption, thermodynamics.*

1. INTRODUCTION

The low costs of the mineral coal and of the petcoke of high sulfur content, in relation to the fuel oil, represent a strong economical attractive for its use. However, the sections that can use them with high degree of absorption of the generated sulfurous compounds are limited. In the face of the growth of the production of heavy petroleum and with high sulfur content and also due to the needed supply of the light derived units, an increasing has occurred in the production of petcoke of high sulfur content, that needs to enlarge its consuming market. So, in this work, it is discussed the use of the petcoke of high sulfur content and its use in the clinker production for the cement industry and it deduces an equation that relates the permitted maximum amount of petcoke of high sulfur content in function of the pyrite content in the raw materials for the production of clinker Portland cement, to maintain the SO2 content inside the exhausted gases of the emission patterns.

1.1. Portland cement production

The clinker is the main raw material for the Portland cement production. The raw materials for the clinker production are the clay and the limestone, that are processed in the system of the rotary kiln, producing the clinker that is milled and it receives additives to form the several Portland cement types (Battye et al, 2000). The average composition of the raw materials for the clinker production is shown in Tab. 1 (PCA, 2001).

Table 1. The average composition of the raw materials for the Portland clinker production.

Component	% weight
$CaCO_3$	78.11
SiO_2	14.67
Al_2O_3	2.53
Fe_2O_3	2.72
$MgCO_3$	1.01
SO_3	0.49
K_2O	0.16
Na_2O	0.09
H_2O	0.23

The system of the rotary kiln is formed by the preheater, calcinator and rotary kiln, and about 60% of the total of fuel is fed in the calcinator (secondary fuel) and the remaining 40% form the primary fuel, feeding the main burner, located in the rotary kiln. The Fig. 1 represents the system of the rotary kiln of production of Portland cement clinker (AWMA, 2006).

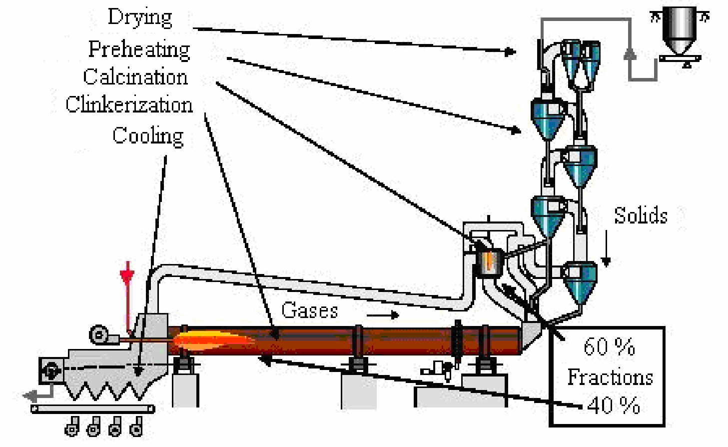

Figure 1. The rotary kiln system of Portland cement clinker production.

The raw materials enter in the system through the preheater in counterflow with the effluent gases of the calcinator and the rotary kiln; in this stage, there are the drying and the clay dehydration. Then, the raw materials go through the calcinator, happening the decomposition of the carbonates in oxides and carbonic gas. The process ends up in the rotary kiln, where the clinkerization reactions happen. So that the formation of the clinker occurs , the temperature of the materials increases in the system, happening the minimum temperature of about 80 ^{o}C, in the preheater and the maxim about 1500 ^{o}C in the rotary kiln, the flame temperature is about 2000 ^{o}C (Battye et al, 2000 and Cembureau, 1999).

1.2. Petroleum coke

Due to the need of production of the lightest fractions of the petroleum, as naphtha, gasoline, kerosene and diesel, the petroleum refineries were adapting themselves, even processing the heaviest petroleum, to assist the consuming market of light and medium products. Thus, the coking process, that converts heavy fractions in light fractions, eventhough producing a solid residue, the petcoke was getting more and more importance in the refineries (ANP, 2003).

Depending on the origin petroleum, the petcoke presents low or high sulfur content. The Tab. 2 displays the composition of a petcoke with high sulfur content.

Table 2. Medium composition and LHV of a petcoke with high sulfur content.

Component	% weight
C	87.90
H	3.51
S	7.47
Ashes	0.33
N	1.61
LHV [kJ/kg]	35,162

The great consumers of petcoke, worldwide, can be seen in Tab. 3 (IEA-COAL, 2004), in which is observed that the cement industry is the greatest consumer of petcoke, followed by the calcination sector and the power plants.

Table 3. The petcoke consuming Market.

Sector	Consumption (%)
Cement	40
Calcination	22
Power plant	14
Iron and steel	7
Heating	1
Others	16

It is of fundamental importance the growth of that consuming market, because the world production of petcoke went from 81 million tons in 2001 (Dynamics, 2004) to 89 million tons in 2005 (EIA, 2007).

1.3. Thermodynamic verification of the absorption of SO_2 in the rotary kiln system

A chemical reaction happens spontaneously, only when its free energy of Gibbs has negative value (Smith and Van Ness, 1987).

The free energy of Gibbs for a chemical reaction, according to Moran and Shapiro (2002) is defined by Eq. (1). The Eq. (2) is deduced from Eq. (1) for a more suitable form to the use of a computer program.

$$\Delta G^0 = \Delta G_P - \Delta G_R \tag{1}$$

$$\Delta G_P - \Delta G_R = \sum n_{Pi}[(h-h_0)-T.(s-s_0)]_{Pi} - \sum n_{Ri}[(h-h_0)-T.(s-s_0)]_{Ri} \tag{2}$$

Being ΔG_P and ΔG_R the variation of free energy of Gibbs of the products and reactants, respectively, h = h - h_0 the enthalpy variation and s = s - s_0 the entropy variation. The values of h and s were calculated or through Eq. (3) and (4), according to Perry et al (1999) or through Eq. (5) and (6), as Carvalho et al (1977), according to the possibility of obtaining of the constant coefficients in those equations; when they weren´t found in those references, were calculated by Neumann Kopp's Rule, according to Leitner (2002).

$$\Delta h = \int_{T_0}^{T} (a + bT - \frac{c}{T^2})dT \tag{3}$$

$$\Delta s = \int_{T_0}^{T} (a + bT - \frac{c}{T^2})\frac{dT}{T} \tag{4}$$

$$\Delta h = AT + B1x10^{-3}T^{-3} + C1x10^{5}T^{-1} + D \tag{5}$$

$$\Delta s = A\ln\frac{T}{T_0} + 2B1x10^{-3}(T - T_0) + \frac{C}{2}1x10^{5}(\frac{1}{T^2} - \frac{1}{T_0^2}) \tag{6}$$

The values of the free energy of Gibbs for the constant absorption reactions in Tab. 4 were calculated by Eq. (2) to (6), using the coefficients as it was mentioned in the previous paragraph, and they are presented in Tab. 4 (Santos, 2007).

1.4. SO_2 Formation and absorption in the rotary kiln system

The Tab. 4 relates the components of the rotary kiln system with the temperatures and the chemical reactions of formation and absorption of SO_2 and oxidation of the pyrite (FeS_2) (PCA, 2001; Zivkovic and Milosavljevic, 1990; and Manovic et al, 2006). In Tab. 4, it´s observed that the values of the free energy of Gibbs for the respective intervals are negative, proving by the thermodynamics the occurrence of the reactions of absorption of the sulfur dioxide in each part of the rotary kiln system.

Table 4. SO_2 formation and absorption in the rotary kiln system, with the values of the free energy of Gibbs (ΔG^o) of the absorption reactions, in the respective temperature intervals.

System component	SO_2 Formation	SO_2 Absorption	
	Reaction	Reaction	ΔG^o x 10^{-3} (kJ/kmol)
Preheater (100 – 550 °C)	$2FeS_2+6O_2 \rightarrow Fe_2O_3+3SO_2+SO_3$	$CaCO_3+SO_2 \rightarrow CaSO_3+CO_2$	- 23.5 a – 21.8
Calcinator (800 – 850 °C)	Secondary fuel → SO_2	$SO_2+CaO \rightarrow CaSO_3$	- 458.3 a - 456.3
		$SO_2+CaO+0{,}5O_2 \rightarrow CaSO_4$	- 192.3 a - 170.5
Rotary kiln (1200 – 1500 °C)	Primary fuel → SO_2	$SO_2+Na_2O+0{,}5O_2 \rightarrow Na_2SO_4$	- 610.0 a – 604.6
		$SO_2+K_2O+0{,}5O_2 \rightarrow K_2SO_4$	- 661.4 a - 638.8
		$SO_2+CaO+0{,}5O_2 \rightarrow CaSO_4$	- 120.5 a - 12.0

In the preheater, the absorption occurs due to the $CaCO_3$ presence in the raw materials. Although, because of the temperature in the calcinator, from 90 to 95% of $CaCO_3$, is decomposed in CaO (Taylor, 1997) and as a result, the SO_2 absorption occurs in reaction with the CaO.

2. RELATIONSHIP AMONG THE SULFUR IN THE PETCOKE AND IN THE RAW MATERIALS CONTENT

As it is observed in Tab. 1 and 2, either the petcoke or the raw materials introduce sulfur in the rotary kiln system. So, it's important to dispose of an equation that selects the type of petcoke in function of the raw materials sulfur content, seeking to maintain the exhausted gases into the limit of the emission parameters. So that,it becomes necessary to know the SO_2 absorption yield in the rotary kiln system.

According to Santos (2007), the values of the SO_2 absorption in the rotary kiln system are presented in Tab. 5.

Table 5. SO_2 absorption (%) in the rotary kiln components.

Equipment	Absorption (%)	Equipment on Fig. 2
Rotary kiln	99.8	FR
Calcinator	88.3	PC
Preheater	36.7	PA

2.1. Modeling for accomplishment of the SO_2 balance in the rotary kiln system

The outline conditions, for the deduction of the relationship among the amount of sulfur contained in the petcoke and the amount of sulfur trioxide in the raw materials are the following ones (Santos, 2007):

a) the petcoke presents p_1% weight sulfur;

b) the primary fuel consumes p_2% of the total mass of petcoke and the secondary fuel consumes p_3% of the total mass of petcoke;

c) the raw presents p_4% in mass of sulfur trioxide;

d) the absorption of sulfur dioxide in the rotary kiln is P_5% and p_5% is the percentage of sulfur dioxide that passes from the rotary kiln to the calcinator;

e) the sulfur dioxide absorption in the calcinator is P_6% and p_6% is the percentage of sulfur dioxide that passes by the pre-calcinator to the preheater;

f) the sulfur dioxide absorption in the preheater is P_7% and p_7% is the percentage of sulfur dioxide that leaves the preheater to the stack;

g) as usually the mill operates in the schedule of cheap electric power, this is a reason to consider it out of the outline conditions;

h) the possible sulfur dioxide absorption in the electrostatic precipitator was also disrespected, which turns the deduction more conservative.

The Fig. 2 presents the simplified flowsheet of the rotary kiln system, in which the outline conditions mentioned above are applied .

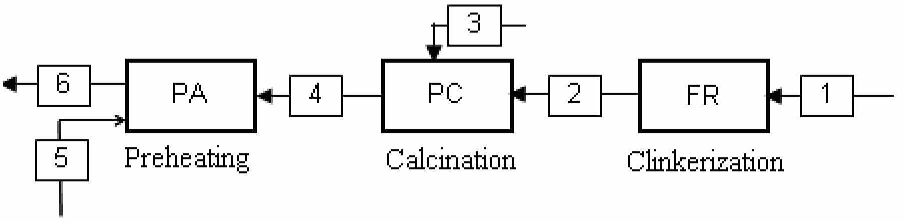

Figure 2. Simplified rotary kiln system flowsheet.

The Tab. 6 identifies the currents and the main equipments of the rotary kiln system, related with the flow and absorption of the sulfur dioxide in the considered system.

Table 6. Characterization of the components of Fig. 2.

Currents/equipments	Characterization
1	SO_2 generated by the primary fuel
2	SO_2 rotary kiln effluent
3	SO_2 generated by the secondary fuel
4	SO_2 calcinator effluent
5	SO_2 generated by the raw materials
6	SO_2 preheater effluent
FR	Rotary kiln (clinkerization in Fig. (1)).
PC	Calcinator (calcination in Fig.(1)).
PA	Four stages preheater (drying and preheating in Fig. (1)).

The deduction will be made according to the following steps (Santos, 2007):

1) the amount of sulfur (S) in the petcoke (CP), in kmol per ton of clinker (CLQ), is calculated by Eq. (7).

$$n(S)_{CP} = m(CP)(\frac{kgCP}{tCLQ}).p_1(\frac{kgS}{kgCP}).(\frac{kmolS}{32kgS}) \tag{7}$$

Simplifying the Eq. (7), it is obtained the Eq. (8).

$$n(S)_{CP} = \frac{p_1.m(CP)}{32}(\frac{kmolS}{tCLQ}) \tag{8}$$

The relationship between the number of kmol of S and the number of kmol of SO_2 is one to one, as presented in Eq. (9).

$$S + O_2 \rightarrow SO_2 \tag{9}$$

Thus, making the substitution in Eq. (8) it is obtained the Eq. (10).

$$n(SO_2)_{CP} = \frac{p_1.m(CP)}{32}(\frac{kmolSO_2}{tCLQ}) \tag{10}$$

2) From Eq. (10) the amounts of SO_2 are obtained, generated by the primary and secondary fuel, respectively according to Eq. (11) and (12).

$$n(SO_2)_1 = \frac{p_2.p_1.m(CP)}{32}(\frac{kmolSO_2}{tCLQ}) \tag{11}$$

$$n(SO_2)_3 = \frac{p_3.p_1.m(CP)}{32}(\frac{kmolSO_2}{tCLQ}) \tag{12}$$

2) the amount of SO_3 generated by the raw materials (CRU) is calculated by Eq. (13).

$$n(SO_3)_5 = m(CRU)(\frac{kgCRU}{tCLQ}).p_4(\frac{kgSO_3}{kgCRU}).(\frac{kmolSO_3}{80kgSO_3}) \tag{13}$$

Simplifying the Eq. (13), it is obtained the Eq. (14).

$$n(SO_3)_5 = \frac{p_4.m(CRU)}{80}(\frac{kmolSO_3}{tCLQ}) \tag{14}$$

From the Eq. (15) it is observed that the relationship between the number of kmol of SO_3 and the number of kmol of SO_2 is one to one.

$$SO_2 + 0{,}5.O_2 \rightarrow SO_3 \tag{15}$$

So, it can be written the Eq. (16) starting from Eq. (14) to (15).

$$n(SO_2)_5 = \frac{p_4.m(CRU)}{80}\left(\frac{kmolSO_2}{tCLQ}\right) \tag{16}$$

4) Considering the absorption of SO_2 in the rotary kiln, in the pre-calcinator and in the pre-heater, the equations from Eq. (17) to (19) will be obtained.

$$n(SO_2)_2 = p_5.n(SO_2)_1 \tag{17}$$

$$n(SO_2)_4 = p_6.[n(SO_2)_2 + n(SO_2)_3] \tag{18}$$

$$n(SO_2)_6 = p_7.[n(SO_2)_4 + n(SO_2)_5] \tag{19}$$

Rearranging the equations from Eq. (17) to (19), the expressions below will be obtained:

4a) $n(SO_2)_4 = p_6.n(SO_2)_2 + p_6.n(SO_2)_3 = p_6.p_5.n(SO_2)_1 + p_6.n(SO_2)_3$

4b) $n(SO_2)_6 = p_3.n(SO_2)_4 + p_7.n(SO_2)_5 = p_7.p_6.p_5.n(SO_2)_1 + p_7.p_6.n(SO_2)_3$
$+ p_7.n(SO_2)_5$

4c) $n(SO_2)_6 = \dfrac{p_7.p_6.p_5.p_2.p_1.m(CP)}{32} + \dfrac{p_7.p_6.p_3.p_1.m(CP)}{32} + \dfrac{p_4.p_7.m(CRU)}{80}$

Containing the expression 4c and putting in evidence the similar terms, the Eq. (20), can be written.

$$n(SO_2)_6 = [\frac{m(CP)}{32}.(p_7.p_6.p_5.p_2 + p_7.p_6.p_3)].p_1 + [\frac{p_7.m(CRU)}{80}].p_4 \tag{20}$$

d) the SO_2 effluent amount of the preheater will be calculated in function of the SO_2 Emission Limit (LE) and of the flow of the effluent gases (V), in Nm^3 (with 7% free O_2) per ton of produced clinker, according to Eq. (21).

$$n(SO_2)_6 = LE\left(\frac{mgSO_2}{Nm^3}\right).V\left(\frac{Nm^3}{tCLQ}\right).\left(\frac{kgSO_2}{10^6\,mgSO_2}\right).\left(\frac{kmolSO_2}{64kgSO_2}\right) \tag{21}$$

Rearranging the Eq. (21), it is obtained the Eq. (22).

$$n(SO_2)_6 = \frac{LE.V.10^{-6}}{64}\left(\frac{kmolSO_2}{tCLQ}\right) \tag{22}$$

e) the Eq. (20) can be written according to the Eq. (23).

$$A = B.p_1 + C.p_4 \tag{23}$$

In the Eq. (23), the variables are p1 and p_4 and the terms constants are:

$$A = \frac{LE.V.10^{-6}}{64}$$

$$B = \frac{m(CP)}{32}.(p_7.p_6.p_5.p_2 + p_7.p_6.p_3)$$

$$C = \frac{p_7.m(CRU)}{80}$$

Separating p1 in the Eq. (23), it is obtained the Eq. (24), turning p1 the dependent variable and p_4 the independent variable.

$$\mathrm{p_1(\%\,S\,in\,CP)} = -\frac{\mathrm{C}}{\mathrm{B}}.\mathrm{p_4(\%\,SO_3\;\;in\,CRU)} + \frac{\mathrm{A}}{\mathrm{B}} \tag{24}$$

As it can be observed, the Eq. (24) represents a straight line, which shows the following characteristic values:

a) for p_4 equals to zero, the p1 value will be the relationship A/B, that will be the ordinate in the origin, representing the maximum value for p_1;

b) for p_1 equals to zero, the p_4 value will be the relationship A/C, that will represent the maximum value for p_4;

c) the derived of p_1 in relation to p_4 (dp_1/dp_4) will be the relationship -C/B, indicating that the function is decreasing in the p_4 interval varying from zero to A/C.

d) the Fig. 3 presents the graph of the suitable function by Eq. (24).

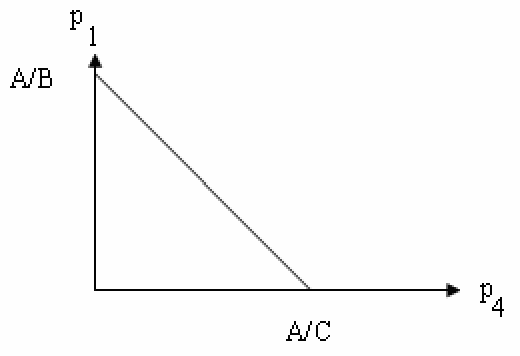

Figure 3. Graph of the suitable function by Eq. (24).

An equation, similar to Eq. (24) can be deduced for the use of a mixture of petcoke and coal, as well as for any mixture of fuels, since that information is considered in the conditions of outline of the modeling.

3. CONCLUSION

To assist the consuming market of having light fractions of petroleum and in the face of the increase of the offer of heavy oils in the supplying market, the refinery managers opted to increase the number of coking units to the petroleum refineries. Thus, there was an increase in the production of petcoke, whose properties depend on the origin petroleum, generating petcoke with low and high sulfur content. The cement industry presents conditions of consuming petcoke with high sulfur content, due to the thermodynamic characteristics of the rotary kiln system. Although that configuration is prejudiced when the raw materials present pyrite, which liberates sulfurous compounds in the preheater, that is the part of the rotary kiln system that presents the smallest absorption yield of those compounds. It seems important the use of a tool that informs the compatibility among the petcoke, the raw materials and the emission parameters. As an option for the selection of the type of petcoke in function of the pyrite content in the raw materials, guaranteeing the control of the emissions, the equation deduced in the present work can be used, allowing the comparison among the theoretical and experimental results.

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