FEASIBILITY STUDY OF THE PORTLAND CEMENT INDUSTRY WASTE FOR THE REDUCTION OF ENERGY CONSUMPTION

Ana Carla de Souza Masselli Bernardo, anacarlasz@unifei.edu.br Mateus Augusto F. Chaib Junqueira, mateus_afcj@yahoo.com.br Ariosto Bretanha Jorge, ariosto.b.jorge@unifei.edu.br Rogério José da Silva, rogeriojs@unifei.edu.br UNIFEI - Federal University of Itajubá, IEM - Institute of Mechanical Engineering Av: BPS, 1303, Itajubá, MG, Brazil – PO Box: 37500-903

Abstract. The Portland cement industry demand a high specific consumption of energy for the production of the clinker. The energy consumption for clinker production varies between 3000 and 5300 kJ/kg of produced clinker. The clinker is produced by blending of different raw materials in order to achieve precise chemical proportions of lime, silica, alumina and iron in the finished product and by burning them at high temperatures. The Portland cement is a mixture of clinker, gypsum and other materials. Due to need of high temperatures, tradition ally the fuels used in the cement industry are mineral coal, fuel oil, natural gas and petroleum coke. The fuel burning in high temperature leads to the formation of the pollutant thermal NOx. The level of emissions of this pollutant is controlled by envir onmental law, thus the formation of pollutants in process need be controled. Moreover, industrial waste has been used by Portland cement industries as a secondary fuel through a technique called co-processing. Materials like waste oils, plastics, waste tyres and sewage sludge are often proposed as alternative fuels for the cement industry. The residues can be introduced as secondary fuel or secondary raw material. For energy conservation in the process, mineralizers are added during the process production of the clinker. The mineralizers promote certain reactions which decrease the temperature in the kiln and improve the quality of the clinker. The adequate quantity of constituents in production process is complex, for maintain in controled level, the qual ity of final product, the operacional conditions of kiln, and the pollutant emissions. The purpose of the present work is to provide an analysis of an optimal production point through of the optimization technique considering, the introduction of the fuels, industrial wastes as secondary fuels, and raw materials, for the reduction of energy in the process of Portland cement production

Keywords: Portland cement, consumption of energy, co-processing, mineralizers, optimization.

1. INTRODUCTION

The Portland cement industry is an energy consumption intensive industry. Clinker production is the most energy intensive stage in cement production, accounting for over 80% of total industry energy use. Clinker is produced by burn in rotative kilns.

The fuels used in the cement industry are mineral coal, fuel oil, natural gas and petroleum coke. Due to the high temperatures of the production process (1450°C), the used fuel should have high calorific power. The fuel burning in high temperature leads to the formation of the pollutant NOx. The emission of this pollutant is controlled by environmental law (Bech and Gundtoft, 1998).

To minimize the environmental impact and cost in the cement production, the industries are using the co-processing technique (Bathy, 1992).

The reaction raw materials and fuels can be changed by the introduction into the process of substances know as mineralizers. The use of mineralizers increases the acceleration of the chemical reactions, promotes the decrease of the fuel consumption and contributes to lowering the NOx thermic pollutant.

In order the reactions occurring at each temperature level, several calculations are needed to obtain a thermal balance.

Due to process complexity, the application of optimization techniques is necessary to a nalyze the variables of the process of Portland cement production. The process of cement production involves countless contradictory objectives and they should be worked as optimization multicriteria.

In this work, the incorporation of mineralizers and wastes and its implication in energy comsunption, SOx and NOx pollutant is investigated.

2- PORTLAND CEMENT PRODUCTION

The most common raw materials used for cement production are limestone, clay, and sand and iron ore as correctives. The chemical composition of cement is of approximately 80% of limestone and 20% of clay. The final

product is obtained in high temperature (1450°C). After burning, the material is suddenly cooled, giving origin to a granular material known as clinker. The clinker is grinding adding 2 to 4% of calcium sulfate. The calcium sulfate has the function of controlling the hardening time of the cement (Rehan and Nehdi, 2005). The Fig. 1 presents a cement production process.



Figure 1: Portland cement production: 1) Limestone quarrying, 2) Clay, 3) Crushing, 4) Classification, 5) Raw Mill, 6)
Homogenization Silo, 7) Pre-heating of Raw Meal in Cyclones, 8) Rotary Kiln, 9) Coal Mill, 10) Coal/Petroleum Coke, 11) Oil, 12) waste, 13) waste, 14) Clinker store, 15) Clinker Mill, 16) Cement Silo and 17) Bagged cement.

During the process of cement production the sílica, Alumina-Iron modulus and the Lime Saturation factor should be controlled. The modulus when controlled represent quality and reduction of consumption of energy in the producti on.

Silica Modulus. The Silica Modulus has influence on the burning of raw materials, clinker granulometry and liquid phase. This modulus is within the interval 2.3 and 2.7. The Silica Modulus (Eq. 1) is obtained as the ratio of the silicates oxide to the sum of the ferric oxide and alumina oxide.

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3} \tag{1}$$

Alumina-Iron Modulus. This relationship influences mainly on the burning process, by acting on speed of the reaction of limestone and silica. The values for this modulus ar e within the interval 1.3 and 2.7.

$$MA = \frac{Al_2O_3}{Fe_2O_2} \tag{2}$$

Lime Saturation Factor. A high factor of lime saturation causes burning difficulties. Acceptable values for this factor are between 0.9 and 1.

$$LSF = \frac{CaO}{2,8SiO_2 + 1,1Al_2O_3 + 0,7Fe_2O_3}$$
(3)

The industry of Portland cement comes increasing its production every year. In 2005, they were produced 2.15 billion ton of cement in the world (CEMBUREAU, 2008). The introduction of residues as fuel or as secondary raw material it already substitutes about 25 percent of the total consumption.

2.1- Pollutants Emissions in the Cement Manufacture

The cement industry is a very pollutant source when the production process is not controlled. Thus, the environmental laws come increasing the control of pollu tant as carbon dioxide, sulfur and nitrogen oxides.

The sulfur are found in the raw material in FeS_2 form (pyrite) and also in the fuel. Depending on the sulfur quantity in the raw material, the use of combustible should to be analyzed for the emission of this pollutant does not overtake the limits allowed by law (Miller *et. al.*, 2001).

Nitrogen oxides, NO_x , is formed during fuel combustion by oxidation of the molecular nitrogen of the combustion air (thermal NO) as well as the nitrogen compounds in the fuels and raw materials (CEMBUREAU, 1999).

In Portland cement manufacturing, conditions favorable for formation of NOx are reached routinely because of high process temperatures.

The fuel cost and environmental standards encouraged cement manufacture world -wide to evaluate in technologies for reduce this emissions. In Brazil, the limit of emission of NOx in Portland cement manufactory is 650 mg/Nm³ (CONAMA, 2006).

2.2-Fuels Used in the Cement Industry

Traditional kiln fuels are coal, petroleum coke, oil and natural gas. Due to the high cost of the derived products of petroleum, the fuels more used in the cement industry today they are petroleum coke and the coal. Materials as waste oils, plastics, shredded residues, waste tyres and sewage sludge are often proposed as alternative fuels for the cement industry. Also, various kinds of municipal waste are offered as fuel nowadays (Kaantee *et. al.*, 2004).

To make possible the use of several of alternative fuels in the Portland cement production, it is necessar y to know the composition of the fuel. The choice is normally based on price and availability. The energy and ash contents are also important, as are the moisture and volatiles contents (Kaantee *et. al.*, 2004). Somehow, they should all be fed into the burning chamber of the process.

3- MINERALIZERS

Mineralizers are inorganic compounds which accelerate the process of reactions in solid phase, liquid phase and solid-liquid interface. They lead to major impacts on the determination of burning zone, the comp osition and formation of clinkers minerals (Kacimi *et. al.*, 2006). The mineralizers are knows the scientific community since the decade 60. However, the use of these substances is told in the decade 80 and 90 (Raina and Janakiraman, 1998).

These compounds may modify the temperature of the first liquid phase formation and or the amount of the melt, change the rate of the reactions occurring in the solid state within the liquid phase or at the liquid -solid interface, alter the viscosity and surface tension of the melt and the affect both crystal growth and morphology (Kolovos *et. al.*, 2005; Molr and Glasser, 1992).

Residues whose composition presents fluorites or phosphates are investigated as mineralizers substances. The phosphogypsium are waste of fertilizers industry.

The selection and use of mineralizer on an industrial scale is primarily to improve quality of clinker or process which depends on its compatibility with other substance feeded in the kiln.

4- MATERIALS AND METHODS

4.1- Reaction Heat Model in the Portland Cement Industry

The high cost of energy and the high consumption of fuel requested in the process of clinkerization are relevant factors for the cement industry. The main objective of the model of reaction heat is to know the difference of the consumption of energy in the cement production with or without the introduction of secundary raw materials and mineralizers.

The chemical composition of the raw material and the amount of inlet (in percentage) in the process of cement production is described in the Tab. 1. The wastes introduced in the process as secondary raw materials is presented in the Tab. 2.

For the model, the conditions of production of Portland cement are:

- Dry rotary kiln with precalciner;
- Clinker production of 26.62 kg/s;
- Initial temperature of the raw materials is 60°C;
- To compose the flow of raw in the entrance of the process, it was made a mixture of raw materials (95 %), of the residue 1 (1%), of the residue 2 (1%) and of the phosphogypsium residue (3%);
- MS between 2.7 and 3.10;
- MA between 1.85 and 3.50;
- FSC between 95.7 and 107.8.

In the literature the used mineralizers reduces the clinkerization temperature by at least 100°C (Raina and Janakiraman, 1998). Based on these facts, the final production temperature with mineralizers was of 1350°C.

Raw	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO
Material					
Limestone	48.94	5.83	1.39	0.62	0.83
Sand	3.13	53.67	22.0	6.48	1.22
Clay	0.94	92.22	3.61	3.36	0.23
Iron Oxide	0.75	3.53	1.89	90.18	0.20

Table 1: Chemical composition of the raw materials for Portland cement production

Table 2: Chemical composition of the secundary raw-materials for Portland cement production .

Composition %	Residue 01	Residue 02	Phosphogypsum
			Residue
Ash	85.06	82.06	-
S	0.33	0.08	-
Cl	0.072	0.082	-
F	12.23	0.401	0.22
SiO_2	18.23	42.03	0.84
Al_2O_3	44.03	16.35	0.04
Fe_2O_3	2.69	12.25	0.39
CaO	5.01	10.41	23.87
MgO	3.02	2.64	0.03
K ₂ O	0.55	1.90	-
Na ₂ O	11.05	1.38	-
SO_4	-	-	54.47

Table 3: Chemical Reactions that occur with or without mineralizers .

Chemical Reactions	Temperature	with	Temperature	without
	Mineralizers	and	Mineralizers and	Residue
	Residue (°C)		(°C)	
Raw materials	60		60	
$MgCO_3 \rightarrow MgO + CO_2$	60 and 660		60 and 660	
$CaCO_3 \rightarrow CaO + CO_2$	660 and 800		660 and 800	
$3CaO + Al_2O_3 \rightarrow C_3A$	1100		1100	
$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow C_4AF$	1100		1100	
$2CaO + SiO_2 \rightarrow C_2S$	1250		1250	
$3CaO + SiO_2 \rightarrow C_3S$	1350		1450	

In this work the introduction of a mixture of four fuels was considered. The introduced fuels are: coal resídue (23.1%), petroleum coque (32.4%), mineral coal (17.0%) and fuel residue (27.5%). In Tab. 4, are showed the chemical compositions and calorific power of the fuels.

The calculation of the enthalpy is given by the following equation:

$$\Delta H = H_{final} - H_{initial}$$

(4)

Where:

H is *enthalpy change* in the strip of studied temperature (H_{final} and H_{initial}), H_{final} is the final enthalpy in the final temperature and H_{initial} is the enthalpy of the system in the initial temperature.

In this work, the study is following the equation :

$$\Delta H = AT + B.10^{-3}T^2 + C.10^5T^{-1} + D \tag{5}$$

Where:

 ΔH is the enthalpy change (Carvalho *et. al.*, 1977), A, B, C, and D are coefficients of the equation that can vary in agreement with the temperature and T is stage of temperature of Portland cement manufacture.

Composition	Residue Coal	Petroleum	Coal	Fuel Residue
%		Coke (Brazil)		
S	0.08	0.73	-	-
Н	2.03	3.16	1.59	3.11
С	69.01	90.76	57.67	69.56
Ν	0.03	1.46	0.34	1.16
Ash	15.32	0.40	10.16	57.21
SiO ₂	40.99	5.15	34.88	7.69
Al_2O_3	13.31	2.90	14.93	7.17
Fe ₂ O ₃	20.95	83.62	37.11	12.10
CaO	12.94	3.72	8.2	8.56
MgO	2.02	0.44	0	1.53
Na ₂ O	0.59	0.29	0.3	0.77
K ₂ O	3.87	0.36	1.1	0.24
P_2O_5	1.44	0.28	-	-
SO ₃	0.91	2.72	-	-
TiO ₂	1.15	0.16	-	-
MnO	1.48	-	-	-
SrO	0.14	0.05	-	-
ZrO_2	0.08	-	-	-
Cl	0.06	-	-	-
ZnO	0.06	-	-	-
MoO ₃	-	-	-	-
V_2O_5	-	0.32	-	-
PCI (Kcal/kg)	6035	8375	4910	3375

Table 4: Chemical composition and calorific power of the Fuels

For each substance of the raw-material, mineralizers, and primary and secondary fuels, a calculation of H is accomplished. The heat of reaction is the sum of all the reactions, considering his value positive or negative. These results of the Eq. (5) are showed in kJ/s or kWatts.

5.1 Numerical Model

5.1.1 - The optimization problem

The purpose of the present work is to provide an analysis of an optimal point through optimization problem with multi-objective functions. The multi-objective functions in the Portland cement production are: production of costs, emissions of SO_2 and NO_x . The function cost of cement production considers the cost of raw materials, residues as secondary raw material, traditional and secondary fuels and energy consumption requested for grinding of clinker.

Multi-objective functions: The raw materials costs can be writen based on the costs of: limestone - x_1 (US\$0.021/kg), clay - x_2 (U\$0.004 \$/kg), sand - x_3 (US\$0.008/kg), iron oxide - x_4 (US\$0.0012/kg), coal - x_5 (US\$0.05/kg), petroleum coke - x_6 (US\$0.225/kg). The residues x_7 and x_8 are considering secundary raw materials. To introduce the residues as secondary raw materials, the cement industries they receive on average \$0.02 per kg burned. The residue x9 (phosphogypsum) are considering the simbolic price US\$0.001/kg. The residues x_{10} and x_{11} are considering residues of the high calorific power. The cement industry receive US\$0.03/kg. The price of the electric power supplied by the concessionary represents a cost of US\$ 62.544/MWh. However the objective function is showed below:

$$f_{1} = 0.021x_{1} + 0.004x_{2} + 0.008x_{3} + 0.0012x_{4} + 0.05x_{5} + 0.225x_{6} - 0.02x_{7} - 0.02x_{8} + 0.001x_{9} - 0.03x_{10} - 0.03x_{11} + 0.062544. \{(5.76.(MS) - 5.82).e^{(-0.2(MS) + 0.98).4}\}$$
(6)

Where MS is the Silice Modulus:

Where MS is the Silica Modulus:

$$MS = \frac{5.83x_1 + 53.67x_2 + 92.22x_3 + 3.53x_4 + 10.16x_5 + 5.15x_6 + 18.23x_7 + 42.03x_8 + 0.84x_9 + 40.99x_{10} + 7.69x_{11}}{2.01x_1 + 6.97x_2 + 28.48x_3 + 92.07x_4 + 52.05x_5 + 86.52x_6 + 46.73x_7 + 28.60x_8 + 0.43x_9 + 34.26x_{10} + 19.27x_{11}} (7)$$

The objective functions of SO₂ and NO_x emissions follow respectively:

$$f_2 = 0.24x_6 + 0.02x_7 + 0.06x_8 + 0.02x_{10}$$
(8)

$$f_3 = 0.06x_5 + 0.47x_6 + 0.007x_7 + 0.32x_{11}$$
(9)

When the problem presents multi-objective functions $f_1(x)$, $f_2(x)$, ..., $f_M(x)$, where $x = (x_1, x_2, ..., x_n)$ is the variable, the fitness function is the weighted sum of objetive functions (Leung, Wang, 2000):

$$fitness = w_1 f_1(x) + w_2 f_2(x) + \dots + w_M f_M(x)$$
(10)

Where $w_1, w_2, ..., w_M$ are nonnegative weights such $w_1 + w_2 + ... + w_M = 1$. In this problem were adopted $w_1 = w_2 = w_3$. This method is called Weighting Objectives Method.

Other method is Global Criterion Method. In this method, the optimal solution is a vector of variables of decision that minimizes some global criterion. The function that describes this global criterion has as more common form:

$$f(x) = \sum_{i=1}^{k} \left(\frac{f_i^0 - f_i(x)}{f_i^0} \right)^s$$
(11)

Where: f_1^0 , f_2^0 , f_3^0 , f_4^0 represent the minimum values of each function objective, found separately.

In this work, the optimal solution was analyzed by the two methods in the algorithm Sequential Quadratic Programming - SQP.

Constraints. The constraints refer to clinker quality, specific heat consumption into kiln, operational order restrictions and modules restrictions of the mixture. The constraints are presented below:

Subject to following constraints:

 $-48.94x_1 - 0.94x_2 - 3.13x_3 - 0.75x_4 - 8.2x_5 - 26x_6 - 5.01x_7 - 10.41x_8 - 23.87x_9 - 12.94x_{10} - 8.56x_{11} - 67$ (12)62 $-5.83x_1 - 92.22x_2 - 53.67x_3 - 3.53x_4 - 34.88x_5 + 4.8x_6 - 18.23x_7 - 42.03x_8 - 0.84x_9 - 40.99x_{10} - 7.69x_{11} - 7.69x_{11}$ 25 (13)19 2 $-1.39x_1 - 3.61x_2 - 22x_3 - 1.89x_4 - 14.93x_5 - 14.25x_6 - 44.03x_7 - 16.35x_8 - 0.04x_9 - 13.31x_{10} - 7.17x_{11} - 9.00x_{11} -$ (14) $1 - 0.62x_1 - 0.23x_2 - 1.22x_3 - 90.18x_4 - 37.11x_5 - 47.5x_6 - 2.69x_7 - 12.25x_8 - 0.39x_9 - 20.95x_{10} - 12.1x_{11} - 12.1x_{11$ 5 (15) $0.83x_1 + 0.23x_2 + 1.22x_3 + 0.2x_4 + 0x_5 + 0.65x_6 + 3.02x_7 + 2.64x_8 + 0.03x_9 + 2.02x_{10} + 1.53x_{11}$ 6.5 (16) $0.403x_1\,81.501x_2 - 23.226x_3 - 245.059x_4 - 105.628x_5 - 228.454x_6 - 107.914x_7 - 35.19x_8 - 0.321x_9 - 0$ $-51.512x_{10} - 44.339x_{11} = 0$ (17) $-1.207x_1 - 83.089x_2 + 11.834x_3 + 208.231x_4 + 84.812x_5 + 193.846x_6 + 89.226x_7 + 23.75x_8 + 0.149x_9 + 37.808x_{10} + 10.000x_{10} + 1$ (18) $+ 36.631 x_{11} 0$ $-0.47x_1 \ 2.53x_2 \ 2.56x_3 \ -268.65x_4 \ -96.4x_5 \ -247.96x_6 \ 35.96x_7 \ -20.4x_8 \ -1.13x_9 \ -49.54x_{10} \ -29.13x_{11} \ 0$ (19) $-0.584x_1 - 3.142x_2 - 13.556x_3 - 115.344x_4 - 33.313x_5 - 105.806x_6 - 40.533x_7 - 0.425x_8 - 0.467x_9 - 13.925x_{10} - 8.56x_{11} - 1000x_{10} - 1000x_{10}$ 0(20) $2937.29x_1 \ -27987x_2 \ -18841.3x_3 \ -7959.52x_4 \ -14146.8x_5 \ -7775.41x_6 \ -10344.5x_7 \ -14393.12x_8 \ -14393.12x_$ $+101.42x_9 - 14122x_{10} - 3198.12x_{11} = 0$ (21) $-3248.17x_1 + 23525.51x_2 + 5798.1\ 6x_3 + 683.01x_4 + 11785.86x_5 + 480.96x_6 + 8621.4x_7 + 11941x_8 - 2146.9x_9 + 11041x_8 + 110$ $+ 11673x_{10} + 2554.01x_{11} = 0$ (22) $20557x_5 + 35064 x_6 + 25267 x_{10} + 14130x_{11} = 3181$ (23)20557x₅ 734.81 (24)35064 x₆ 1030.64 (25)25267 x₁₀ 734.81 (26)14130x₁₁ 874.78 (27) $0.2 -0.1x_1 -0.3x_2 -0.5x_3 -2.07$ (28) $0.31 - 0.3x_1 - 5x_2 - 1x_3 - 1.76$ (29)

The content of raw-materials such as CaO, SiO₂, Al₂O₃, Fe₂O₃ and MgO are limited in the composition of the clinker. The equations (12) and (16) represent the operational order restrictions in the cement production. The content of CaO must be between 62 and 67% to equations (12). The content of SiO₂ must be between 19 and 25% to Equation (13). The amount of Al₂O₃ must be between 2 and 9% to Equation (14). The equations (15) refer the amount of Fe₂O₃ between 1 and 5%. The maximum content of magn esium is limited in 6.5% Eq. (16).

The equations (17) to (22) represent the restrictions of the module s of control of the mixture. This control guarantees the clinker quality. The total feeding of fuels must satisfy the specific heat consumption, presented in restrictions (2 3) and (27). The restrictions of Eq. (28) represent the acid oxide in the raw material. The restrictions of Eq. (28) refer to the alkalis content in the raw material.

In this work, the objective functions (6), (8) and (9) is solved using Sequential Quadratic Programming (SQP).

6- RESULTS AND DISCUSSIONS

Portland cement production consumes great amount of thermal energy. The results show that the use of mineralizers and secondary raw materials decreases the energy consumption in the cement kiln.

With the introduction of the mineralizer (phosphogypsum), secundary raw material and secundary fuel are necessary reactions for the cement production happen in the temperature of 1350°C. Besides, the decrease of temperature promotes the reduction of the clinkerization temperature and consequently the reduction of thermal NOx. Another advantage is the introduction of fuels with smaller calorific power. The Tab. 5 summarizes the results obtained from heat balance in the cement industry.

Temperature	Heat reaction with mineralizers and wastes	Heat reaction without mineralizers and wastes (kJ/s)
	(kJ/s)	
60 and 660°C	49550	52640
660 and 800°C	15550	69490
800 and 1200°C	38300	38530
1200°C and 1350°C	-7621	-
1200°C and 1450°C	-	-13660
Sum	143949	147000

Table 5: The values of heat balance in the cement industry

In this work, the non-linear problem with multi-objective functions and constraints were presented. The compositions of the raw materials, fuels and mineralizers are taken as variables.

For the Global criterion method, the cost presents to be larger than in the Weighting Objectives Method.

The method consideration of weights is the pioneer of the methods and it is influenced by the user. The global criterion doesn't suffer the user's interference and therefore the result is better.

Comparing the results without the matter introduction excels secondary, secondary fuels and mineralizers, the cost is smaller. In the Tables (6) and (7) summarizes the results obtained from the optimization of the objective functions, Eq. (6) Eq. (8) and Eq. (9), with the corresponding constraint equations.

Table 6: Results of optimization for Weighting Objectives Method				
Functions	Functions f_1 (US\$/ton of clinker) f_2 (kg/ton of clinker) f_3 (kg/ton of clinker)			
Results	3.56	0.0023	0.0579	

Functions	f1 (US\$/ton of clinker)	f ₂ (kg/ton of clínker)	f ₃ (kg/ton of clinker)
Results	3.56	0.0023	0.0579

Table 7: Results of optimization for Global Criterion Method				
Functions	ctions f_1 (US\$/ton of clinker) f_2 (kg/ton of clínker) f_3 (kg/ton of clínker)			
Results	3.71	0.0036	0.0463	

Also, the amount of fuels used for clinker production with mineralizers was smaller than in the case without mineralizers, due to the decrease in the maximum clinkering temperature.

The use of this type of wastes has been well established, as can be seen in a recent work, in which the alternative use of massive amounts of phosphogypsum as a mineralizer was presented from Ozturk et. al., (2000).

The introduction of residues as raw material and fuel doesn't cross the limit of emissions of pollutant in the atmosphere. The amount of SO_x and NO_x is very small.

In this work it was not considered the actual heavy metals in the residues. The introduction of these residues in larger amounts should be analyzed for not concentrating these metals in the cement.

Besides cost issues, mineralizers had lowered the kiln temperature and also had promoted the formation of C ₃S, therefore improving the quality of the clinker. Finally, it must be pointed out that the use of certain type of secondary fuels, such as scrap tires, could also promote the decrease in the formation of pollutants, for example, the thermic NO $_{\rm x}$.

The combination of mineralizers and secondary raw materials and fuels could lead to a better solution for the Portland cement production.

For future works, the study of heavy metals in the residue should be investigated and on optimization problem will include another technique of global optimization.

7- CONCLUSIONS

However, in the industry due to countless operational restrictions, the reduct ion of consumption of heat is smaller. The reduction of the temperature allows the consumption of fuel to be smaller. Also, with the reduction of the

temperature, the use of fuels with small calorific powder is possible, and the reduction of Thermic NOx is verified in the process of Portland cement production.

The chemical compositions and burnability of these raw materials and fuels (secondary) they were appropriate. The final cost and SOx and NOx emissions are smaller. These results are acceptable for the environmental laws.

The study also indicates that a combination of mineralizers and residues show the most promising results. For future works, the study of heavy metals in the residue should be investigated.

In the numerical model, the final production cost is smaller when the introduce the secondary fuels and raw materials. The mineralizer (phosphogypsum) present other advantages, such as the lowering of the kiln temperature, the decrease the consumption fuels, and the improvement in the quality of the c linker.

8. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by FAPEMIG – Fundação de Amparo à Pesquisa do Estado de Minas Gerais.

9. REFERENCES

- Carpio, R. C., 2005. "Optimization in the co-processing of waste in the cement industry comprising cost, quality and environmental impact" PhD Thesis. Federal University of Itajubá UNIFEI, Institute of Mechanical Engineering.
- Carvalho, J. L. R.; Assis, P. S.; Figueira, R. M.; Camilo, R. D.; Campos, V. F. 1997. "Thermodynamic dates for metallurgists" Federal University of Minas Gerais. Department of Metallurgic Engineering. Belo Horizonte.
- CEMBUREAU, 1999. "Best available techniques for the cement industry". A contribution from the European cement industry to the exchange of information and preparation of the IPPC BAT REFERENCE. Document for the cement industry.

CONAMA - National Council of Environment. Resolution nº 382, Published in 12/26/2006.

- Environmental Protection Agency EPA 2000. Contract n°. 68-D98-026 Work Assignment n°. 2-28, EC/R Project n°. ISD-228. "NO_x control technologies for the cement industry". Final report.
- Giménez-Molina, S., Blanco-Varela, M. T., 1995. "Solid state phases relationship in the CaO-SiO, Al₂O, CaF₂-CaSO₄ system". *Cement and Concrete Research*, vol. 25, n. 4, 870–882.
- Kacimi, L.; Simon-Masseron, A.; Ghomari, A.; Derriche, Z., 2006 "Reduction of clinkerization temperature by using phosphogypsum". Journal of Hazardous Materials, 137, 129-137.
- Khurana, S.; Banerjee, R.; Gaitonde, U., 2002. "Energy balance and cogeneration for a cement plant". Applied Thermal Engineering, 22, 485-494.
- Kolovos, k.; Tsivilis, S.; Kakali, G., 2005. "SEM examination of clinkers containing foreign elements". Cement and Concrete Research, 27, 163 170.
- Miller, F. M.; Young, G. L.; Seebach, M. von., 2001. "Formation and techniques for control of sulphur oxide and other sulphur compounds in Portland cement kiln systems". Portland Cement Association.
- Mohr, G. k.; Glasser, F. P., 1992. "Mineralizers, modifiers and activators in the clinkering process". 9th International Congress on the Chemistry of Cement.
- Ozturk, A.; Suyadal, Y.; Oguz, H., 2000. "The formation of belite phase by using phosphogypsum and oil shale". Cement and Concrete Research, 30, 967-971.
- Silva, R, J., 1994. "Energetic analysis of production plants of Portland cement". PhD Thesis, State University of Campinas UNICAMP, Faculty of Mechanical Engineering. Campinas SP, Brazil.
- Sprung, S., 1993. "Effect of energy consumption and environmental control measures on clinker properties". Third Brazillian Congress on Portland Cement.
- Szabó, L.; Hidalgo, I.; Ciscar, J. C.; Soria, A., 2006. "CO₂ emission trading within the European Union and Annex B countries: the cement industry case". Energy Policy, 34, 72-87.
- Rehan, R.; Nehdi, M., 2005. "Carbon dioxide emissions and climate change: policy implications for the cement industry". Environmental Science & Policy, 8, 105–114.
- Rasul, M. G.; Widianto, W.; Mohanty, B., 2005. "Assessment of the thermal perf ormance and energy consevation opportunities of a cement industry in Indonésia". Appliede Thermal Engineering , 25, 2950-2965.

10. RESPONSIBILITY NOTICE

The author(s) is (are) the only responsible for the printed material included in this paper.