

REDUCTION IN THE CONSUMPTION OF THERMAL ENERGY IN ROTARY KILNS OF A CEMENT PLANT BY THE USE OF MINERALIZERS AND THE IMPLICATIONS IN THE EMISSION OF NO_x

Ana Carla de Souza

anacarlaz@hotmail.com

UNIFEI – Federal University of Itajubá, IEM – Institute of Mechanical Engineering
Av: BPS, 1303, Itajubá, MG, Brazil – PO Box: 37500-903

Maria Luiza Grillo Renó

malureno@yahoo.com.br

UNIFEI – Federal University of Itajubá, IEM – Institute of Mechanical Engineering
Av: BPS, 1303, Itajubá, MG, Brazil – PO Box: 37500-903

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

Ariosto Bretanha Jorge

Ariosto.b.jorge@unifei.edu.br

UNIFEI – Federal University of Itajubá, IEM – Institute of Mechanical Engineering
Av: BPS, 1303, Itajubá, MG, Brazil – PO Box: 37500-903

Abstract. *In the Portland cement industry, the specific consumption of heat for the fabrication of the clinker can be very high, depending on the type of kiln being used. This work investigates the use of substances that operate as mineralizers in the process, leading to: i) a reduction in the temperature of clinkerization, ii) a decrease in the temperature of the flame, iii) the possibility for the use of different fuels with low calorific power, and iv) increase in the quality of the clinker. The co-processing of several types of industrial waste in the clinker kilns permits the partial substitution of primary fuels, as well as the introduction of several mineralizer substances. For this case, an optimum point of operation can be found through optimization techniques, by considering the mineralizers in the formation of the clinker, the environmental restrictions, and the final production cost. The results obtained in this work show that the use of the mineralizers CaF₂ (0.50%) and CaSO₄ (1.0), decrease the necessary temperature in the interior of the rotative kiln in approximately 100°C. The reduction of the flame temperature leads to a significant decrease in the formation of thermic NO_x and, consequently, in the emissions of this pollutant in the atmosphere, which are common in these kilns.*

Keywords: *Cement Industry, Co-processing, Mineralizers, Economy of energy, Emissions of pollutants*

1. INTRODUCTION

The Portland cement industry is an energy consumption intensive industry. The energy consumption for clinker production varies between 3000 and 5300 kJ per kilogram of produced clinker (Rasul *et.al.* 2005, Khurana *et. al.* 2002, Sprung 1993). In order, to decrease more than the energy consumption is used dry rotary kiln with preheater and precalciner (Szabó, *et. al.* 2006).

Traditionally, the fuels used in the cement industry are mineral coal, fuel oil, natural gas and petroleum coke. Such fuels must present specific flame characteristics and constituents in order not to influence the stage of clinker production or clinkerization. The fuel burning in high temperature leads to the formation of the pollutant NO_x. The emission of this pollutant is controlled by environmental law (Bech and Gundtoft, 1998; Greer, 1988).

In order to minimize the environmental cement production, the application of the co-processing technique has been in recent years. In this co-processing, several secondary fuels are frequently used in the cement industry, such as used tires, residues of wood, sludge of re-refinement of lubricant oils, coal dust, tire scraping, carbon residue, solvent and sludge of paint (Bathy, 1992).

Also, due to manufacture process complexity, the chemical reactions in the process should be controlled specially regarding the addition of wastes should be analyzed. In this process control, secondary fuels can be used and to increase the elements or chemical compounds by changing the reactions.

The reactions raw materials and fuels can be changing by the introduction into process of substances know as mineralizers. The use of mineralizers decreases the acceleration of the chemical reactions, promotes the fuel consumption and contributes for low emission the pollutant thermic NO_x.

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. The cement cost is to be minimized by introduction of waste and mineralizers while keeping valid all constraint equations, such as the ones regarding quality, environmental and, operations restrictions.

In this work, the incorporation of mineralizers, such as CaF_2 and CaSO_4 and its implication in NO_x reduction is investigated. To minimize the final cost, while the constraint equations were included to form the feasible region.

2- PORTLAND CEMENT PRODUCTION

The chemical composition of cement is of 80% of limestone and approximately 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 ground adding 2 to 4% of calcium sulfate. The calcium sulfate has the function of controlling the hardening time of the cement (British Geological Survey, 2005; Rehan and Nehdi, 2005).

After additions of gypsum, fly ash, granulated blast furnace slag or limestone dust to compose different kinds of cement, the cement is sacked (ABCP, 2005). The Figure 1 presents a Cement Production Process.

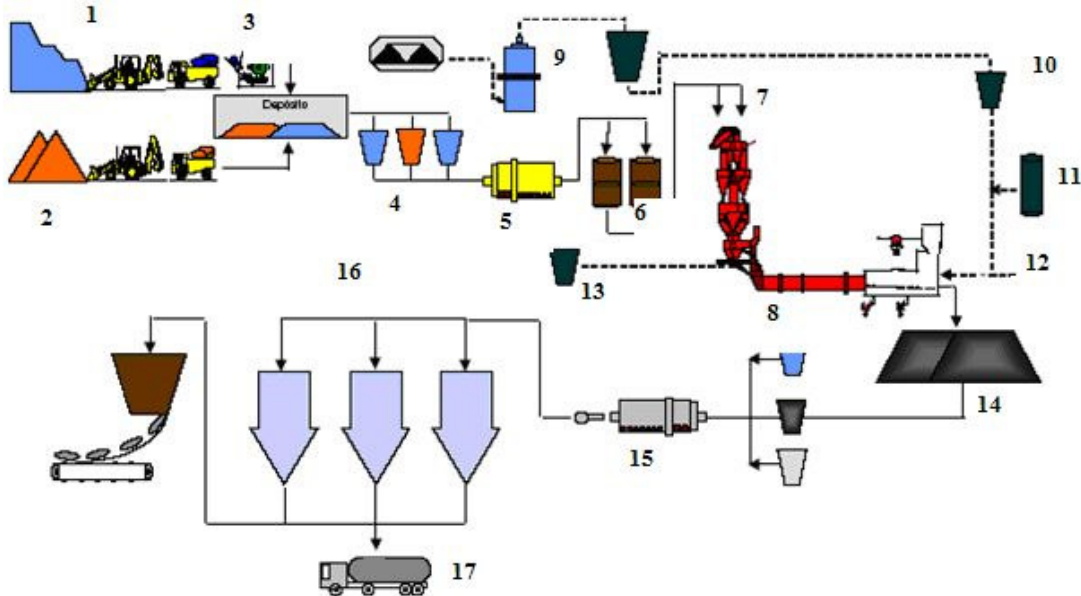


Figure 1: Portland cement production: 1) Limestone quarrying, 2) Clay, 3) Crushing, 4) Classification, 5) Raw Mill, 6) Homogenization Silo, 7) Pre-heating of Raw Meal in Cyclones, 8) Rotary Kiln, 9) Coal Mill, 10) Coal/Petroleum Coke, 11) Oil, 12) waste, 13) waste, 14) Clinker store, 15) Clinker Mill,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

The industry of Portland cement comes increasing its production every year. In 2004, they were produced 2 million ton of cement in the world (British Geological Survey, 2005).

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 pollutant as Carbon Dioxide, sulfur and Nitrogen Oxides. With the raw material burning, CO_2 is liberated to form calcium oxide, main raw material for obtainment of the composed of the Portland cement. Carbon Dioxide emission also occurs with the fuels burning.

The emission of this pollutant promotes the effect greenhouse gas increase in the atmosphere. In the cement industry, for each tonne of Portland cement produced releases approximately 1 tonne of CO_2 (Rehan and Nehdi, 2005 *apud* Worrell *et. al.*, 2001).

The sulfur oxides are found in the raw material in SO_2 form 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).

2.1.1- Nitrogen Oxide Emission

Nitrogen oxide, NO , 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 NO_x are reached routinely because of high process temperatures. Essentially all NO_x emissions associated with Portland cement manufacturing are generated in cement kilns.

Thermal NO_x is formed by the homogeneous reaction of oxygen and nitrogen in the gas phase at high temperatures. In the overall reaction mechanism proposed by Zeldovich (1946) *apud* EPA *et. al.*, (2000), the two important steps in NO formation are given as:



where k_f are the rate constants for the reactions shown. The high activation energy of reaction, 76.5 kcal/mol, means that this reaction is the most temperature sensitive. An equilibrium reaction of NO with O₂ further results in NO₂ formation.

Because of the high temperatures involved in the burning or clinker formation step, thermal NO_x formation provides the dominant mechanism for NO_x formation in cement manufacturing (EPA *et. al.*, 2000).

To reduce NO_x emissions from a pyroprocessing system to a certain controlled level, two basically different methods are available:

- Modify the existing process;
- Maintain the existing process while adding a separate gas cleaning unit for the exhaust gas (secondary reduction measures).

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 NO_x in Portland cement manufactory is 560 mg/Nm³ (DN 26, 1998).

2.2-Fuels Used in the Cement Industry

Traditional kiln fuels are mineral coal, petroleum coke, oil and natural gas. Materials like waste oils, plastics, auto shredded residues, waste tyres and sewage sludge are often proposed as alternative fuels for the cement industry. Also, all kinds of slaughterhouse are offered as fuel nowadays (Kaantee *et. al.*, 2004).

Recently, the use of petroleum coke fuel is common. This fuel has high calorific power, and can be used as traditional fuel in the cement industry.

To make possible the use of several of alternative fuels in the Portland cement production, it is necessary 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; Mokrzycki, and Bochęczyk, 2003). Somehow, they should all be fed into the burning chamber of the process.

In table 1, several fuels of interest to the Portland cement industry and their composition are listed. These fuels were used in model calculations of thermal balance.

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 composition and formation of clinkers minerals (Kacimi *et. al.*, 2006).

The mineralizers are known to 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; Puertas *et. al.* 1996).

The effect of these mineralizers on the clinker properties was also studied by many researchers, which determined the influence of mineralizers on the equilibrium phases in the CaO-SiO₂-Al₂O₃ system in determined temperature (Molina and Varela, 1995), the influence of minor components in the clinker (Molr and Glasser, 1992), the use of mineralizers in the Vertical Shaft kiln (VSK) technology (Raina and Janakiraman, 1998), study of influence of the pair mineralizers CaF₂ and CaSO₄ in white Portland cement (Puertas *et. al.*, 2002; Varela *et. al.*, 1997) and others. The mineralizing properties of the compounds CaF₂ and CaSO₄ have already been described in the literature. Their properties are different when they are added separately or jointly in the raw materials.

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).

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 the given kilnfeed.

The use of mineralizers promotes the decrease of the necessary temperature to form the clinker. In this case, the mineralizers can contribute to the reduction of thermal NOx.

Table 1. Chemical composition in mass (%) of the fuels used for Portland cement production.

Component	Coal (%)	Petroleum Coke (%)	Tires uses (%)
C	63.9	87.90	72.15
H	3.6	3.51	6.74
S	4.6	7.06	1.23
O	0.9		9.67
N	1.8	1.2	0.36
Cl			0.149
Total Ash	24.9	0.33	9.85
Ash Components Distribution			
CaO	1.03	7.74	12.75
SiO ₂	9.32	8.84	23
Al ₂ O ₃	5.08	1.85	11.46
Fe ₂ O ₃	7.21	4.06	3.55
MgO	0.44		2.95
Alkalis	0.85		
ZnO	0.04		37.5
Cd	0.001		
CrO	0.008	0.14	
NiO	0.008	34.43	
Pb	0.027		
TiO ₂	0.0004		5.87
Hg			
As	0.00017		
V	0.0648		
LHV [kJ/Kg]	25.392	35.162	38.340

4- REACTION HEAT MODEL IN THE CEMENT INDUSTRY

Recently, the cement industry is investigating new technologies to reduce the consumption of fuel and consequently of final cost of production. The energy consumption of kilns with suspension pre heaters is much smaller, than the others types of process (Szabó *et. al.*, 2006).

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 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 table 2.

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

Raw material	Percentage
CaCO ₃	64.96
Al ₂ O ₃	5.50
Fe ₂ O ₃	2.99
SiO ₂	19.81
MgCO ₃	2.46
SO ₃	1.26
Na ₂ O	0.5
K ₂ O	1.13
Cl ₂	0.031
CaF ₂	0.775
CaSO ₄	1.55
Sum	≈100

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

- Dry rotary kiln with pre-calciner;
- Clinker production of 34.72 kg/s;
- Initial temperature of the raw-material is 60°C;
- In the precalciner, 60% of the total fuel (petcoke and tires) for the cement production are consumed;
- The secondary (tires) fuel used in the process is introduced in the pre-calciner

- The mineralizers were introduced in the inlet of the rotative kiln.

In the literature, the mineralizers use reduces in 100°C the clinkerization temperature. Based on these facts, the final temperature of production with mineralizers was of 1300°C.

The process of clinker production happens in four stages: such as raw material introduction, pre-calcination, burns of the raw-material in the rotative kiln and cooling. In these stages of the process, the temperatures are different and controlled to guarantee the final quality of the clinker. The temperature differences in each stages of the production process and the main chemical reactions that happen are showed in the table 3.

Table 3: The chemical reactions and temperature that occur the quaternary compounds of the clinker

Temperature of	Chemical Reaction
About 800°C	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
Between 800°C and 1200°C	$2\text{CaO} + \text{SiO}_2 \rightarrow \text{C}_2\text{S}$
Between 1095 and 1205°C	$3\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{C}_3\text{A}$ $4\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{C}_4\text{AF}$
To 1260°C and 1455°C	$3\text{CaO} + \text{SiO}_2 \rightarrow \text{C}_3\text{S}$

Source: Silva (1994)

Considering the temperature variation to form the reactions, one study the variability of the enthalpy is accomplished. In the thermodynamics terms, enthalpy can be calculated to determine the reaction heat in each temperature stage showed in the table 3. In table 4, are showed the temperature and reactions that happen with or without mineralizers.

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

$$\Delta H = H_{final} - H_{initial} \quad (3)$$

Where:

ΔH 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:

$$\Delta H = AT + B.10^{-3}.T^2 + C.10^5.T^{-1} + D \quad (4)$$

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.

Table 4. Chemical Reactions that occur with or without mineralizers

Chemical Reactions	Temperature with Mineralizers (°C)	Temperature without Mineralizers (°C)
Raw materials	60	60
$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	60 and 660	60 and 660
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	660 and 800	660 and 800
$3\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{C}_3\text{A}$	1100	1100
$4\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{C}_4\text{AF}$	1100	1100
$2\text{CaO} + \text{SiO}_2 \rightarrow \text{C}_2\text{S}$	1250	1250
$3\text{CaO} + \text{SiO}_2 \rightarrow \text{C}_3\text{S}$	1350	1450

To accomplish the calculation of the modelling of the reaction heat with or without mineralizers, the raw-material, mineralizers and secondary fuels percentages, were calculated in the unit kmol/s of clinker, considering a production of 34.72 kg/s of clinker.

For each substance of the raw-material, mineralizers, and primary and secondary fuels, a calculation of ΔH is accomplished. The reaction heat is the sum of all the reactions, considering his/her value positive or negative. These results of the Eq. (3) are showed in kJ/s or kWatts. The heat balance was realized in the MathCad program.

5- NUMERICAL MODEL

5.1- Description of the optimization problem

The main objective is to obtain the raw materials, fuels and mineralizers optimum costs composition necessary to manufacture the clinker employing the optimization algorithms.

The relations used to express the raw mix burnability are described as: Silica Modulus, Alumina-Iron Modulus, and Lime Saturation Factor. An optimization procedure concerning this mixture is intended to guarantee a better stability and operation of the rotary kilns, and also a reduction in the energy consumption. Several restrictions are considered in the optimization models, as detailed below (Carpio, 2005):

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. 5) is obtained as the ratio of the silicates oxide to the sum of the ferric oxide and alumina oxide.

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3} \quad (5)$$

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 are within the interval 1.3 and 2.7.

$$MA = \frac{Al_2O_3}{Fe_2O_3} \quad (6)$$

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

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

The data for the objective function of the optimization problem (Eq. 9) was taken from Table 1, where the chemical composition of the fuel. In the table 5 are showed the percentile values of the several oxides present in limestone x_1 , clay x_2 , sand x_3 , iron ore x_4 , fluorspar x_8 , and gypsum x_9 .

Table 5. Chemical composition of raw materials, in mass (%)

Raw Materials	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O
Limestone	50.66	5.04	1.19	0.67	0.78	0.1	0.1
Clay	1.23	61.62	16.59	0.01	-	0.3	0.3
Sand	1.13	93.00	2.87	1.2	0.10	0.5	0.5
Iron Ore	0.71	7.6	1.13	82.97	-	-	-
Fluorspar	45.13	18.33	2.06	0.78	0.30	-	-
Gypsum	23.81	18.55	1.4	0.83	0.97	34.99	-

The optimization of raw materials should consider rotary kilns operation stability, the quality of the clinker produced, the composition minimum cost, and the electricity consumption. The optimization problem has an objective function with restrictions. The objective function is given by (Souza *et. al.*, 2005 *apud* Carpio, 2005):

$$C = \sum_{i=1}^n p_i x_i + pA \exp(BS) \quad (8)$$

Where:

C is clinker production cost (US\$/ton), taking into consideration raw materials costs as well the energy consumption requested for grinding. The first term (linear terms) represents materials cost which comprises raw materials and fuels (primary and alternative).

The second term (nonlinear) represents the unit electricity cost p (US\$/kWh) times the grinding energy consumption in kWh/ton. S (cm²/g) represents a specified Blaine specific surface area. The parameters A and B depend on the clinker composition

These equation can be rewrite based on the costs of mineral coal x_5 (US\$30,32/10³ kg), petroleum coke x_6 (US\$27,2/10³ kg), limestone (US\$0.93/10³ kg), clay (US\$0.54/10³ kg), sand (US\$1.54/10³ kg), iron ore (US\$0.77/10³ kg), fluorspar (US\$152/10³ kg), gypsum (US\$60/10³ kg). The values of cost of the compositions Fluorspar and Gypsum are considered when acquired as pure substances. Scrap tires x_7 are considered as revenue for the cement industry, with

an income of US\$32/ton. 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:

$$\begin{aligned} \text{Min } f(x) = & 0,93x_1 + 0,54x_2 + 1,54x_3 + 0,77x_4 + 30,32x_5 + 27,2x_6 - 32x_7 + 152x_8 + 60x_9 \\ & 0.062544 * \{ (5,76(MS) - 5,82) * e^{(-0,2(MS)+0,98)*4} \} \end{aligned} \quad (9)$$

Where MS is the Silica Modulus

$$MS = \frac{5,04x_1 + 61,62x_2 + 93x_3 + 7,6x_4 + 9,32x_5 + 1,93x_7 + 18,33x_8 + 18,55x_9}{1,86x_1 + 25,6x_2 + 4,07x_3 + 84,1x_4 + 12,29x_5 + 0,92x_7 + 2,84x_8 + 2,23x_9} \quad (10)$$

Subject to following constraints:

$$50.66x_1 + 1.23x_2 + 1.13x_3 + 0.71x_4 + 1.03x_5 + 0.93x_7 + 45.13x_8 + 23.83x_9 \geq 62 \quad (11)$$

$$50.66x_1 + 1.23x_2 + 1.13x_3 + 0.71x_4 + 1.03x_5 + 0.93x_7 + 45.13x_8 + 23.83x_9 \leq 67 \quad (12)$$

$$5.04x_1 + 61.62x_2 + 93x_3 + 7.6x_4 + 9.32x_5 + 1.93x_7 + 18.33x_8 + 18.55x_9 \geq 19 \quad (13)$$

$$5.04x_1 + 61.62x_2 + 93x_3 + 7.6x_4 + 9.32x_5 + 1.93x_7 + 18.33x_8 + 18.55x_9 \leq 25 \quad (14)$$

$$1.19x_1 + 16.59x_2 + 2.87x_3 + 1.13x_4 + 5.08x_5 + 0.79x_7 + 2.06x_8 + 1.40x_9 \geq 2 \quad (15)$$

$$1.19x_1 + 16.59x_2 + 2.87x_3 + 1.13x_4 + 5.08x_5 + 0.79x_7 + 2.06x_8 + 1.40x_9 \leq 9 \quad (16)$$

$$0.67x_1 + 9.01x_2 + 1.20x_3 + 82.97x_4 + 7.21x_5 + 0.13x_7 + 0.78x_8 + 0.83x_9 \geq 1 \quad (17)$$

$$0.67x_1 + 9.01x_2 + 1.20x_3 + 82.97x_4 + 7.21x_5 + 0.13x_7 + 0.78x_8 + 0.83x_9 \leq 5 \quad (18)$$

$$0.78x_1 + 0.10x_3 + 0.44x_5 + 0.12x_7 + 0.30x_8 + 0.97x_9 \leq 6.5 \quad (19)$$

$$0.76x_1 + 2.74x_2 + 83.64x_3 - 185.83x_4 - 18.95x_5 - 0.19x_7 + 11.8x_8 + 13.42x_9 \geq 0 \quad (20)$$

$$-0.02x_1 + 7.5x_2 - 82.01x_3 + 219.47x_4 + 23.86x_5 + 0.56x_7 - 10.66x_8 - 12.53x_9 \geq 0 \quad (21)$$

$$0.32x_1 + 4.88x_2 + 1.31x_3 - 106.73x_4 - 4.29x_5 + 0.63x_7 + 1.05x_8 + 0.32x_9 \geq 0 \quad (22)$$

$$0.62x_1 + 7.74x_2 + 0.37x_3 + 222.89x_4 + 14.39x_5 - 0.45x_7 + 0.05x_8 + 0.84x_9 \geq 0 \quad (23)$$

$$36.36x_1 - 176.15x_2 - 236.83x_3 - 71.83x_4 - 32.03x_5 - 4.8x_7 - 3.59x_8 - 24.82x_9 \geq 0 \quad (24)$$

$$-34.77x_1 + 195.86x_2 + 263.27x_3 + 79.89x_4 + 35.70x_5 + 5.44x_7 + 9.01x_8 + 30.23x_9 \geq 0 \quad (25)$$

$$25392x_5 + 34436x_6 + 32100x_7 = 3181 \quad (26)$$

$$32100x_7 \leq 795.33 \quad (27)$$

$$25392x_5 + 34436x_6 \leq 2386 \quad (28)$$

$$0.05x_5 + 0.07x_6 + 0.01x_7 \leq 0.02 \quad (29)$$

$$0.1x_1 + 0.3x_2 + 0.5x_3 \geq 0.2 \quad (30)$$

$$0.1x_1 + 0.3x_2 + 0.5x_3 \leq 2.07 \quad (31)$$

$$0.3x_1 + 5x_2 + 1x_3 \geq 0.31 \quad (32)$$

$$0.3x_1 + 5x_2 + 1x_3 \leq 1.76 \quad (33)$$

$$1x_8 \geq 0.005 \quad (34)$$

$$1x_9 \geq 0.01 \quad (35)$$

The equations (11) and (19) represent the operational order restrictions in the cement production. The content of raw-materials such as CaO, SiO₂, Al₂O₃, Fe₂O₃ are limited in the composition of the clinker. The content of CaO must be between 62 and 67% to equations (11) and (12). The content of SiO₂ must be between 19 and 25% to Equation (13)

and (14). The amount of Al_2O_3 must be between 2 and 9% to Equation (15) and (16). The equations (17) and (18) refer the amount of Fe_2O_3 between 1 and 5%. The maximum content of magnesium is limited in 6.5% Eq. (19).

The equations (20) to (25) represent the restrictions of the modules 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 (26) and (28). The restriction for the sulphur is presented in Eq. (29). The value is based in the environmental law European. The restrictions of Eq. (30) and (31) represent the acid oxide in the raw material. The restrictions of Eq. (32) to Eq. (33) refer to the alkalis content in the raw material. The restrictions Eq. (34) and (35) represent the percentage of mineralizers CaF_2 and $CaSO_4$.

In this work, the nonlinear programming problem defined by Eqs. (9) and (10) is solved using Sequential Quadratic Programming (SQP). The main idea in SQP is to obtain a search direction by solving a quadratic program, that is, a problem with a quadratic objective function and linear constraints (Nash and Sofer, 1996).

6- RESULTS AND DISCUSSIONS

Portland cement production consumes great amount of thermal energy. The use of secondary fuels and the mineralizers introduction are waking up interest in the scientific community. The results show that the use of mineralizers decreases the energy consumption in the cement kiln. Table 6 summarizes the results obtained from heat balance in the cement industry.

The mineralizers are added together with the primary and secondary fuels in the temperature rate 800 and 1200°C.

Table 6: The values of heat balance in the cement industry

Temperature	Heat reaction with mineralizers (kJ/s)	Heat reaction without mineralizers (kJ/s)
60 and 660°C	66200	66200
660 and 800°C	15550	15550
800 and 1200°C	4524	40530
1200°C and 1350°C	-6934	-
1200 and 1450	-	-19360
Sum	79340	102920

In Table 6, the values of reaction heat in the temperatures 60, 660°C and 800°C are equal. This results is due to mineralizers absence in the process. The difference among the heat reactions with or without mineralizers is very expressive.

With the introduction of the compositions CaF_2 and $CaSO_4$, to necessary reactions for the cement production happen in the temperature of 1.350°C. In this case, the reduction of temperature of the process is 100°C, maintaining the quality of the cement. Also, the resulting chemical reactions of the incorporation of the mineralizers in the process, it allows an increase of the enthalpy, guaranteeing the variation of the formation heat in function of the temperature.

Besides, the mineralizers use promotes the reduction of the clinkerization temperature and consequently the reduction of thermal NOx. These results are promising perspective.

The introduction of tires as secondary fuel also favors the reduction of the formation of Thermal NOx. This result is provable to be burns her partially of the fuel to happen in the pre-calciner in against current to the exhaustion gases. This result is due to it burns partially of the fuel that it generates CO. The carbon monoxide reacts with NOx formed in the rotative kiln and it produces N_2 (Signoretti and Silva, 2006).

As disadvantage, the fluoride can cause the retard of the setting time of the Portland cement (Hills *et. al.*, 2002).

In the Table 7 summarizes the results obtained from the optimization of the objective function, Eq. (9), with the corresponding constraint equations. All results are presented in US\$ per ton of clinker.

In the optimization model, the obtained results show that the cost of electric energy for the clinker production presented a small improvement with the addition of mineralizers. 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.

Table 7: Cement Production cost with or without mineralizers

Portland Cement	Fuels	Raw Materials	Electricity	Sum
With Mineralizers (CaF_2 and $CaSO_4$)	1.0958	2.6528	3.538153	7.2874
Without Mineralizers	1.2415	1.2913	3.538284	6.0698
With Mineralizers in the form of waste	1.0958	1.3078	3.538153	5.9418

From Table 7, one can see that the raw materials cost increased significantly, above 100%, when mineralizers were added, due to the market price of the mineralizers that was used in the formulation. With this, the final cost presented an increase of US\$ 1.2176 per ton of clinker, when comparing the sum in the first and second lines of this table. Using, as secondary fuels, industrial wastes containing mineralizing agents, could reduce this cost. The residues of the industries of fertilizers and of aluminum they are rich in CaSO_4 and CaF_2 . 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).

Mineralizers proceedings from industrial wastes decrease the final cost. With a symbolic price for each mineralizers (US\$ $1/10^3$ kg) results a final cost of US\$ 5.9418 per ton of clinker. This cost can be reduced still more when provides income to the cement industry. Therefore the addition of mineralizers is advantageous when acquired from industrial wastes.

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_x .

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

7- CONCLUSIONS

The use of mineralizers allows the decrease of amount of heat to produce Portland cement as presented in the Table 6. The introduction of CaF_2 and CaSO_4 decreases the clinkerization temperature in 100°C . These results are satisfactory.

However, in the industry due to countless operational restrictions, the reduction 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 NO_x is verified in the process of Portland cement production.

The chemical compositions and burnability of these raw-materials and fuels (secondary or alternative) they were appropriate. The final free CaO in the clinker is less than 2%.

The study also indicates that a combination of mineralizers show the most promising results. For future works, the introduction of secondary fuels and residues with mineralizers should be investigated.

Selection of mineralizer and the mode of addition demand a careful investigation to determine what is appropriate for plant practice, as various process and material parameters need to be optimized.

In the numerical model, due to the current cost of the mineralizers, in special the CaF_2 , which is very expensive, the final production cost is very high when mineralizers are added. Further research is needed for know mineralizers proceedings from industrial wastes (phosphogypsum is a by-product of the fertilizers or residues of the aluminum production) or less expensive mineralizers. The mineralizers present other advantages, such as the lowering of the kiln temperature, the decrease the consumption fuels, and the improvement in the quality of the clinker.

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