STUDY OF THE IMPACT OF THE CO-PROCESSING TECHNIQUE IN THE PORTLAND CEMENT INDUSTRIES DUE TO THE RELATED ENVIRONMENTAL CONSTRAINTS

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Abstract. The main raw materials used for the Portland cement production are the limestone, the sand, the clay and iron ore. These raw materials supply the oxides: CaO, SiO₂, Al_2O_3 and Fe_2O_3 ; necessary for the production of the clínquer. 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. Due to need of high temperatures, traditionally the fuels used in the cement industry are mineral coal, fuel oil, natural gas and petroleum coke. 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. Others metallic oxides are found in the Portland Ciment in smaller amounts. These oxides are classified as trace elements. The metallic oxides are originating from of raw materials and primary fuels. The industrial residues used in the co-processing can contain these oxides, increasing her concentration in the clinker and altering her quality. The introduction of industrial wastes can increase the concentration of heavy metals in the clínker. Due to her volatility, this can be emitted for the atmosphere generating environmental damages. The introduction of residues in the Portland cement production should be controlled. Due to the process of cement production to be complex, the variables should be controlled. With the introduction of residues it increases the number of variables. So that the process is accomplished with safety, optimization techniques are necessary. The adequate quantity of constituents in production is necessary for maintain in controled level, the quality 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 considering the introduction of the heavy metals.

Keywords: Portland Cement, Co-processing, Industrial Waste

1. INTRODUCTION

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.

To minimize the environmental impact and cost in the cement production, the industries are using the co-processing technique (Bathy, 1995).

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, 2009). In Brazil, the cement production in 2009 was of 51.5 million tons (SNIC, 2010).

The introduction of residues as fuel or as secondary raw material it already substitutes about 25 percent of the total consumption.

Due to process complexity, the application of optimization techniques is necessary to analyze the variables of the process of Portland cement production. In this work, the incorporation of industrial wastes and its heavy metals is investigated.

2. PORTLAND CEMENT PRODUCTION

The Portland cement production is result the raw materials such as: limestone, clay and chalk. The collected raw materials are selected, crushed, ground, so that the resulting mixture has the desired fineness and chemical composition for delivery to rotative kiln. The raw materials enter in the kiln and they react forming the compounds C_3A , C_4AF C_2S and C_2S that create the clinker, the main component of the Portland cement (Silva, 1994). The final product is obtained in high temperature (1450°C). In the Portland 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 production. 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, 2010). The Figure 1 presents a Cement Production Process.



Figure 1. Stages of the Portland Cement Production: 00- Natural deposit of ores and crushering, 01- storage of limestone; 02 and 03- additives storage; 04- Raw mill; 5- Raw materials Storage; 06- Preheaters; 07- Cyclone; 08- Rotary kiln; 09- Clínker Cooler; 10- Storages of clinker and gypsium; 11- Fuels; 12-Cement Storage; 13- Package and expedition.

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).

The use of blended cements is a particularly attractive efficiency option since the intergrinding of clinker with other additives not only allows for a reduction in the energy used (and carbon emissions) in clinker production, but also corresponds to a reduction in carbon dioxide emissions in calcination as well.

The fuel cost and environmental standards encouraged cement manufacture world-wide to evaluate in Technologies for reduce this emissions.

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 slaughter house 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 Bochëczyk, 2003).

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 knows the scientific community since the decade 60. However, the use of these substances is told in the decade 80 and 90 (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).

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. OPTIMIZATION TECHNIQUE

In this work, the incorporation of mineralizers and wastes and its implication in Portland cement Production is analyzed by the optimization technique CRSI.

Among the population set-based direct search methods for global optimization problems, Controlled Random Search Algorithms (CRSA) are probably the less known ones in the engineering community. In comparison with Genetic, Differential Evolution and Swarm Particle Algorithms, there are relatively few works about CRSA. However, their ease of implementation, fastness and good results obtained in some complex practical problems suggest that these algorithms could be used as a general purpose global optimization technique for continuous functions.

Since the basic CRSA was proposed by Price (1977), some studies have been done in order to improve its robustness and convergence rate. Since the basic CRSA was proposed, some studies have been done in order to improve its robustness and convergence rate. Ali *et al.* (1997) presented a summary of the principal versions of CRSA developed until 1997 and also proposed a new version named CRS6/CRSI. All these CRSA versions were compared in various test problems and the proposed version appeared to be the most promising in that work. Lately, Ali and Törn (2004) compared the CRSI with Genetic and Differential Evolution Algorithms in several benchmark test problems. The results have shown that the CRSI would deserve improvements for increasing its robustness in finding global optimizers. But in terms of function evaluations, the versions CRS6/CRSI already proved to be competitive.

The basic CRSA for minimization can be described in six steps as follows (adapted from Ali. et. al., (1977):

1. Generate an initial population P of N random points in S: $P = \{x1, ..., xN\}$. Compute the function values of these points in an indexed way. Determine the worst point, h, and the best point, l, i.e., those points in P with the highest and the lowest function values, fh and fl, respectively. If a stopping criterion is already satisfied, then stop (for example, stop if $fh - fl < \varepsilon$, where ε is a given tolerance).

2. Generate a trial point p for replacing the worst point, h.

3. If p is infeasible ($p \in S$), go to step 2 (or alter p to be feasible).

4. Evaluate fp = f(p). If p is unsatisfactory ($fp \ge fh$), go to step 2.

5. Update the set P by replacing the current worst point by the trial point: $(P \leftarrow P \cup \{p\} / \{h\})$. Find h and fh in new P. If fp < fl, then set p, fp as new l, fl.

6. If a stopping criterion is satisfied, stop; else go to step 2.

The two main differences among the available CRSA versions are related to (i) the generation mode of the Trial point (step 2) and (ii) the optional access to a local search phase whenever the best point is the newest in the population

(when fp < fl in step 5). It should be noted that all versions assume that N >> n and it is typically suggested N = 10(n + 1).

5. MODELLING THE RESTRICCIONS OF PORTLAND CEMENT PRODUCTION

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.

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.

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

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 are within the interval 1.3 and 2.7.

$$MA = \frac{Al_2O_3}{Fe_2O_3} \tag{2}$$

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)

In the Portland cement production many variables are involved in the process. The cement production with secondary fuel and raw materials should be accomplished in a controlled way.

Chemical Composition	Known Form
3CaO.SiO ₂	C_3S
$2CaO.SiO_2$	C_2S
$3CaO.Al_2O_3$	C ₃ A
4CaO.Al ₂ O ₃ .Fe ₂ O ₃	C_4AF

Table 1: Main composed of the Portland cement production

To obtain a reduced cost of production without harming the quality and the environment, optimization techniques can be used. The data for the objective function of the optimization problem (Eq. 4) was taken from Table 2, where the cost /tonne are showed. In the table 3 are showed the percentile values of the principal oxides of the variables present in the process. In the table 4 and table 5 are showed the chemical compositions and ash in the residues and fuels.

Table 2: Cost of the raw materials and traditional and secondary fuels

Variables	Cost (US\$/ton)
X ₁ - Limestone	60.18
X ₂ - Sand	33.63
X ₃ - Clay	53.10
X ₄ - Iron Oxide	177.00
X ₅ - Mineral Coal	354.00
X ₆ - Petroleum Coke	283.20
X ₇ - Residue 01	-35.40
X ₈ - Residue 02	-35.40
X ₀₉ - Phosphogypsium	1.77
X ₁₀ - Fuel Residue	54.87
X_{11} – Fine of Charcoal	247.80

Variables	Ash (%)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
X ₁ - Limestone	-	48.94	5.83	1.39	0.62
X ₂ - Sand	-	3.13	53.67	22.00	6.48
X ₃ - Clay	-	0.94	92.22	3.61	3.36
X ₄ - Iron Oxide	-	0.75	3.53	1.89	90.18
X ₅ - Mineral Coal	7.73	0.51	4.21	1.50	0.99
X ₆ - Petroleum Coke	2.59	0.677	0.84	0.47	0.42
X ₇ - Residue 01	84.43	10.41	42.03	16.35	12.25
X ₈ - Residue 02	74.14	5.01	18.23	44.03	2.69
X ₀₉ - Phosphogypsium	-	23.87	0.84	0.04	0.39
X ₁₀ - Fuel Residue	49.83	8.56	7.69	7.17	12.10
X_{11} – Fine of Charcoal	29.31	5.82	16.39	2.39	2.81

Table 5. Chemical composition of the variables for 1 or thand cement production	Table 3: Chemical con	mposition of the	variables for	Portland cement	production
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Table 4: Chemical composition of the variables for Portland cement production

Composition %	Residue 01	Residue 02	Residue
			Phosphogypsium
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 5: Chemical composition of the variables for Portland cement production

Composition	Coal Residue	Petroleum	Petroleum Mineral Coal	
%		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 ₂ O 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 ₂ O ₅	-	0.32	=	-
PCI (Kcal/kg)	6035	8375	4910	3375

$$Min f(x) = 60.18x_1 + 33.63x_2 + 53.30x_3 + 177.00x_4 + 354.00x_5 + 283.20x_6 - 35.40x_7 - 35.40x_8 + 1.77x_9 - 54.87x_{10} + 247.00x_{11} + 0.1663\{(5.76(MS) - 5.82)e^{(-0.2(MS) + 0.98)^{*4}}\}$$
(4)

$$MS = \frac{5.83x_1 + 53.67x_2 + 92.22x_3 + 3.53x_4 + 4.21x_5 + 0.84x_6 + 42.03x_7 + 18.23x_8 + 0.84x_9 + 7.69x_{10} + 16.39x_{11}}{2.01x_1 + 28.48x_2 + 6.97x_3 + 92.07x_4 + 2.49x_5 + 0.55x_6 + 28.60x_7 + 46.72x_8 + 0.43x_9 + 19.27x_{10} + 5.2x_{11}}$$
(5)

The equations (06) and (13) 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 (06) and (07). The content of SiO₂ must be between 19 and 25% to Equation (08) and (09). The amount of Al₂O₃ must be between 2 and 9% to Equation (10) and (11). The equations (12) and (13) refer the amount of Fe₂O₃ between 1 and 5%. The maximum content of magnesium is limited in 6.5% Eq. (14).

The equations (15) to (20) represent the restrictions of the modules of control of the mixture. This control guarantees the clinker quality.

The restriction for the sulphur is presented in Eq. (21). The value is based in the environmental law European.

The restrictions of Eq. (22) and Eq. (23) refer to the alkalis content in the raw material.

The total feeding of fuels must satisfy the specific heat consumption, presented in restriction (25).

The percentage of phosphogypsium is showed in the restrictions (26).

$$48,94x_1+3,13x_2+0,94x_3+0,75x_4+0,51x_5+0,67x_6+10,41x_7+5,01x_8+23,87x_9+8,56x_{10}+5,82x_{11} \ge 62$$
(6)

$$48,94x_1+3,13x_2+0,94x_3+0,75x_4+0,51x_5+0,67x_6+10,41x_7+5,01x_8+23,87x_9+8,56x_{10}+5,82x_{11} \le 68$$
(7)

$$5,83x_1 + 53,67x_2 + 92,22x_3 + 3,53x_4 + 4,21x_5 + 0,84x_6 + 42,03x_7 + 18,23x_8 + 0,84x_9 + 7,69x_{10} + 16,39x_{11} \ge 19$$
(8)

$$5,83x_1 + 53,67x_2 + 92,22x_3 + 3,53x_4 + 4,21x_5 + 0,84x_6 + 42,03x_7 + 18,23x_8 + 0,84x_9 + 7,69x_{10} + 16,39x_{11} \le 25$$
(9)

$$1,39x_1+22,0x_2+3,61x_3+1,89x_4+1,50x_5+0,47x_6+16,35x_7+44,03x_8+0,04x_9+7,17x_{10}+2,39x_{11} \ge 2$$
(10)

$$1,39x_1+22,0x_2+3,61x_3+1,89x_4+1,50x_5+0,47x_6+16,35x_7+44,03x_8+0,04x_9+7,17x_{10}+2,39x_{11} \le 6,5$$
(11)

$$0,62x_1+6,48x_2+3,36x_3+90,18x_4+0,99x_5+0,42x_6+12,25x_7+2,69x_8+0,39x_9+12,10x_{10}+2,81x_{11} \ge 2$$
(12)

$$0,62x_1+6,48x_2+3,36x_3+90,18x_4+0,99x_5+0,42x_6+12,25x_7+2,69x_8+0,39x_9+12,10x_{10}+2,81x_{11} \le 5$$
(13)

$$0,83x_1 + 1,22x_2 + 0,23x_3 + 0,20x_4 + 0,09x_5 + 0,132x_6 + 2,64x_7 + 3,02x_8 + 0,03x_9 + 1,53x_{10}0,29x_{11} \le 6,5$$
(14)

$$-7,33x_{1}-25,76x_{2}+85,83x_{3}-227,42x_{4}-3,51x_{5}-1,92x_{6}-46,63x_{7}-126,60x_{8}-0,49x_{9}-52,05x_{10}+0,27x_{11}\geq0$$
(15)

$$4,68x_1 + 14,68x_2 - 87,03x_3 + 196,89x_4 + 2,51x_5 + 1,56x_6 + 35,19x_7 + 107,91x_8 + 0,32x_9 + 44,34x_{10} - 2,35x_{11} \ge 0$$
(16)

$$-1,25x_{1}-0,56x_{2}-1,56x_{3}-237,24x_{4}-1,96x_{5}-1,00x_{6}-26,52x_{7}+34,62x_{8}-1,33x_{9}-35,18x_{10}-7,45x_{11}\geq0$$
(17)

$$-1,63x_{1}-9,80x_{2}-0,11x_{3}+122,27x_{4}+0,33x_{5}+0,31x_{6}+6,31x_{7}-39,05x_{8}+0,68x_{9}+15,22x_{10}+2,81x_{11}\geq0$$
(18)

$$-4,60x_{1}-209,95x_{2}-287,54x_{3}-85,74x_{4}-14,61x_{5}-2,70x_{6}-143,93x_{7}-103,45x_{8}+21,01x_{9}-31,98x_{10}-48,20x_{11}\geq0$$
(19)

$$-0,62x_{1}+186,40x_{2}+255,24x_{3}+75,93x_{4}+12,91x_{5}+2,32x_{6}+126,62x_{7}+91,28x_{8}-21,33x_{9}+27,43x_{10}+42,14x_{11} \ge 0$$
(20)

$$0,03x_5 + 0,02x_6 + 0,08x_7 + 0,07x_8 + 0,12x_{11} \le 1$$
(21)

(26)

$$0,36x_{1}+0,85x_{2}+0,01x_{3}+0,55x_{4}+0,60x_{5}+0,20x_{6}+1,38x_{7}+11,05x_{8}+0,77x_{10}+0,15x_{11} \le 1$$
(22)

$$0,78x_1 + 3,40x_2 + 0,02x_3 + 0,16x_4 + 2,06x_5 + 0,80x_6 + 1,90x_7 + 0,55x_8 + 0,24x_{10} + 3,0x_{11} \le 1$$
(23)

$$0,83x_1 + 1,0x_2 + 0,01x_3 + 0,04x_4 + 1,26x_5 + 1,05x_6 + 0,08x_7 + 0,33x_8 + 0,27x_{11} \le 5$$
(24)

$$20557x_5 + 35064x_6 + 15525x_{10} + 25267x_{11} \le 3600 \tag{25}$$

 $x_{9} \leq 1.0$

6. RESULTS AND DISCUSSIONS

In this work, the non-linear problem with objective function with linear constraints were presented. The results show that is possible the use of mineralizers and secondary raw materials in the Portland Cement Production. With the introduction of the phosphogypsium, secundary raw material and secundary fuel promotes the reduction of the clinkerization temperature and consequently the introduction of fuels with smaller calorific power (industrial waste). The best value for the production cost and the amount of each variable is presented in the Table 6.

Table 06: Results of Optimization											
\mathbf{X}_{1}	\mathbf{X}_{2}	X ₃	X_4	X_5	X ₆	X_7	X ₈	X9	X ₁₀	X ₁₁	Cost US\$
1.2176	0.0301	0.0918	0	0.0001	0	0.0623	0.1302	0.05	0	0.0003	242.00

The technique CRSI is applicable to minimize the cost of Portland Cement Production. The results show that is possible the use of mineralizers and secondary raw materials in the Portland Cement Production.

With the introduction of the mineralizer (phosphogypsium), secundary raw material and secundary fuel are necessary reactions for the cement production happen in the temperature of 1.350°C (Bernardo et. al., 2008). Besides, the decrease of temperature promotes the reduction of the clinkerization temperature and consequently the reduction of thermal NOx.

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