

# STUDY OF THE VIABILITY OF THE CO-PROCESSING OF INDUSTRIAL RESIDUE IN KILNS FOR CLINKER PRODUCTION IN THE CEMENT INDUSTRY

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**Abstract.** *The residues co-processing technology in clinker kilns is not just limited to its thermal destruction, because in these kilns, the fuel and the raw materials get mixed together. This is very important to determine the characteristics of the fuel and their constituents, it is important to have control on the flame characteristics, fuel calorific value and also on the ashes incorporation to the clinker. For this control to happen, it is necessary to analyze the chemical composition of the alternative fuels, as well as the presence of trace components, including heavy metals, and the substitution percentage. This work analyzes the viability of burning alternative fuel (solvent residue) and to what extent it is possible to substitute traditional fuels, such petroleum coke in kiln of clinker production, during co-processing of industrial residue. Questions relating to the feeding rate of the residue in the burner, calculation of the time residence of the gases in the kiln, burning temperatures and the estimate of the concentration of heavy metals in the gases in the exhaustion of the process, will be addressed.*

**Keywords:** *cement industry, co-processing, alternative fuels, pollutant, heavy metals*

## 1. INTRODUCTION

The Co-processing industrial wastes in rotary kiln of clinker production appeared as an appropriate technology for the treatment certain types of industrial residues. The first burning tests of residues in these types of kilns were accomplished in the 70's in United States. Actually, this technique has been used thoroughly at several countries of the world.

The process consists basically of substituting a part of the traditional fuel (mineral coal, fuel oil, petroleum coke and natural gas) by an industrial residue with characteristics under pre-established patterns for operational and environmental questions. In this way one has an economy of energy resources, and on the other hand, treatment and final disposal of hazardous residues.

The residues that still possess considerable energy content can be reused as alternative, secondary or complementary fuels. This application is called co-processing or co-incineration due to the occurrence of two processes in just, which are the burning of residue and its thermal treatment.

This residue treatment process presents a great deal of technical-economic and environmental viability; therefore, it allows the use of residues as alternative fuels and as raw materials for manufacture of clinker that is the main constituent of the Portland cement. The process success is up to an efficient control of the flame temperature and the process of heat transfer as well as the control of the correct dosage of materials used as raw materials by trying to get high values of destruction efficiency and removal (Silva, 1994).

Although, extremely adjusted and with sufficiently inferior costs to the conventional incineration (up to 10 times), the co-processing of residues does not have to be used indiscriminately. Therefore, many of them are not useful for burning in this process. Making the process possible through the thermal destruction of a determined residue with co-processing must be made case by case where it is necessary to evaluate the residue physical and chemical features and its compatibility with the clinkerization process. The relative environmental limitations to the atmospheric emissions, to safety and risk related to handling and to packaging and transport of the residues must be observed. Moreover, the fact that part of the residues is incorporated to the clinker must be taken into consideration.

Besides the issues reported previously, the co-processing of residues depends on other factors that must be taken into consideration when using this technique such as the type of process, type of equipment used, point of fuel feeding in the process. Thus, a system of kiln endowed with preheater and precalciner where 60% of the required thermal energy for the process comes from a secondary burning in the combustion chamber of the precalciner, where temperatures between 1273 and 1473 K take place. In the main burner of the kiln, the remaining combustion occurs, where the temperatures vary between 2073 and 2273 K. This way, this kiln type will present a behavior different from endowed kilns with preheaters whose residue burning is carried out almost in its totality in the burner of the rotary kiln, making it possible for a small one percentile (10% to 20%) of alternative fuel to be burned in the elevation duct U.S. EPA (2000).

The kilns with preheater/precalciner are smaller when compared to the kilns only with preheaters. The lower burning temperature in the precalciner and the short time residence of the gases inside this kiln type due to the smaller length can make it possible that some toxic compounds in the alternative fuel may not be completely degraded, and then being dragged in the gaseous current and thrown to atmosphere, causing environmental pollution.

This work analyzes the viability of burning alternative fuel (solvent residue) and the possibility to substitute traditional fuels, such as petroleum coke in kiln of clinker production, during co-processing of industrial residue. Questions relating to the feeding rate of the residue in the burner, calculation of the time residence of the gases in the kiln, burning temperatures and the estimate of the concentration of heavy metals in the gases in the exhaustion process will be addressed.

## 2. THE USE OF SECONDARY AND RESIDUAL FUELS

The sustainability of the planet is the largest challenge that belongs to humanity now, due to the crescent use of resources in the richest countries and to the Asian giants' development. Therefore, it is a priority to find alternative production solutions that allow creating goods and services today without minimizing the resources of the future and with a minimum global environmental impact of the several segments of the productive chain. Starting from this need, the regulator agency, also influenced by the social pressure by a better life quality, is creating laws and regulations that demand solutions for final disposition of the different types of generated residues. The decrease of the emission of the Greenhouse gases foreseen in the Protocol of Quioto, the complex world energy situation and the need of rendering an integrated policy of administration of residues imply that, in Brazil, concrete measures are taken similar to the ones that are already applied in other countries in these matters. Therefore, the valorization of residues as alternative fuels or as secondary raw materials in the cement industry has been an normal practice in Brazil for some years in several states, based on the effective legislation that regulates this activity (by CONAMA - Conselho Nacional do Meio Ambiente at federal level and for the competent organs in the state field).

The use of industrial residues as alternative secondary fuels has been a viable route for the industries to reduce their production costs and to reduce the consumption of fossil fuels. Besides, for the residue-generating industries, it is the expected solution for the disposition demanded by the environmental legislation.

Nowadays, the spectrum of residues co-processed in the cement industry is varied. One can add to the list of alternative fuels since the 80's, the used oils, sludge refine of lubricating oils, petroleum coke, used tires, chip of tires, solvents residues, sludge paintings, urban residues and treatment sewerage.

## 3. ALTERNATIVE FUELS

Several types of alternative fuels besides possessing calorific value, they can still have in their ashes, sources of raw materials. The fuels used by the cement industry should possess a minimum calorific value, specific characteristics of flame and of constituent that do not affect the quality of the clinker and, consequently, of the cement. For its high consumption, these should be selected carefully in term of their elementary chemical composition, calorific values and costs. In the last years, with the increasing use of less noble fuels in the rotary kiln and even the co-processing of hazardous residues, it has been having a larger concern with the operational and environmental problems being brought up by such technique. This has been taking the researchers to worry about the presence of smaller components, not only in the traditional fuels, but also in the residual alternative fuels. The limits of emissions imposed by the environmental legislation of several countries demand a careful study of the current effects of the use of these fuels. At the same time, operational problems can appear, such as: formation of collages, covering deterioration, instability of operation of the kiln, etc. The ashes originating from fuel burning are usually incorporated to the clinker, and they should be foreseen in the moment of the grinding of the raw, or of the paste, the swinging of the mixture, in order to avoid quality problems.

The fuels with conditions to be used in the rotary kiln, besides being economically viable, they should still possess compatible physiochemical characteristics with the demands of combustion of the process. Their chemical components should have little or any negative influence on the final composition of the clinker and on its quality starting from the products formed during the combustion.

The Table 1 presents the calorific value of some fuels and materials used as fuels.

Table 1. Comparative examples of calorific value approximate of some fuels

|                         | <b>HCV</b>   | <b>LCV</b>   |
|-------------------------|--------------|--------------|
|                         | <b>kJ/kg</b> | <b>kJ/kg</b> |
| Used tires              | 33030        | 31505        |
| Coal                    | 28970        | 27792        |
| Residues derived fuels. | 25820        | 22592        |
| Wood                    | 20700        | 19200        |
| Municipal residues      | 15120        | 13290        |

Source: Adapted Hansen (2003).

### 3.1. Petroleum coke

When the raw oil is refined, the lightest fractions are removed, remaining a residual oil of smaller value. In some refineries, this residual oil is processed again, in order to produce a larger amount of light products, generating the petroleum coke as residue. The production of petroleum coke has been increasing in function of the increase of the processing of heavy petroleum and of the need of larger amount of light fractions. Depending on the petroleum that the petroleum coke was processed from, it can present tenors of sulfur from 0.7 to 7.5% influencing its market value making its use attractive. The petroleum coke is used mainly as fuel in systems of steam generation and in the cement industries. The green petroleum coke is used in clinker production, as only fuel, or in mixtures with mineral coal, vegetal coal, natural gas, fuel oil or used tires. The chemical compositions and the LCV of six types of petroleum coke are presented in Tab. 2. In the calculations of this work, the petroleum coke type 1 was used in the mixture with solvent residue.

Table 2. Typical composition and lower calorific value of the 6 petroleum coke

| Element     | Petcoke 1<br>% (dry basis) | Petcoke 2<br>% (dry basis) | Petcoke 3<br>% (dry basis) | Petcoke 4<br>% (dry basis) | Petcoke 5<br>% (dry basis) | Petcoke 6<br>% (dry basis) |
|-------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| C           | 87.85                      | 87.9                       | 89.4                       | 88.4                       | 88.5                       | 85.8                       |
| H           | 3.51                       | 3.51                       | 3.6                        | 3.7                        | 1.94                       | 3.5                        |
| O           | 1.1                        | 1.1                        | 0                          | 0                          | 0                          | 0                          |
| S           | 7.47                       | 7.08                       | 4.02                       | 6.16                       | 6.00                       | 5.85                       |
| N           | 1.61                       | 1.51                       | 1.88                       | 1.56                       | 1.63                       | 1.7                        |
| V           | 0.0507                     | 0.0819                     | 0.2570                     | 0.1390                     | 0.0899                     | 0.1830                     |
| Co          | 0.00091                    | -                          | 0.00019                    | 0.00038                    | 0.00061                    | 0.00031                    |
| Mo          | 0.0007                     | -                          | 0.00014                    | 0.00173                    | 0.00263                    | 0.00166                    |
| Mn          | 0.00051                    | -                          | 0.000005                   | 0.00026                    | 0.00171                    | 0.00061                    |
| LCV (kJ/kg) | 34450                      | 34350                      | 34500                      | 34350                      | 32500                      | 33400                      |

Source: Adapted Commandré and Salvador (2005)

### 3.2. Solvents residues

Chemical industries produce large amounts of residues of organic solvents. Some of these solvents cannot be recovered. These residues are usually incinerated in incinerator of hazardous residues, or used as secondary fuel in kilns of clinker production in substitution to the fuels that are traditionally used in the burning process such as mineral coal and fuel oil. Depending on the present chemical compounds in the residues of solvents used, a positive or negative ecological impact can be promoted regarding the emissions of resulting pollutants from their burns. Among the advantages of co-processing solvents residues in the industry of the cement, it can be mentioned: the smallest consumption of total energy of the process, once it is not necessary expenses with electricity for grinding the fuel solid; better use of the heat generated in the process, because with the use of residues of solvents, complementary operations as drying and heating of the traditional fuel are not necessary like in the case of the use of coal and the fuel heavy oil. Seyler *et al* (2005).

The elementary composition and LCV for the solvent residue co-processed in cement plants of Switzerland used in the calculations of this work presented in Tab. 3.

Table 3. Typical composition of solvent residue incinerated in the Swiss plants Holcim.

| Element     | Solvent residue (% wt)<br>(Ethanol with traces of heavy metals) |
|-------------|---|
| C           | 52.2  |
| H           | 13.0  |
| O           | 3.48  |
| Cu          | 0.01  |
| Ni          | 0.01  |
| Zn          | 0.04  |
| LCV (kJ/kg) | 26900   |

Source: Seyler *et al* (2005)

#### 4. HEAVY METALS IN THE CEMENT PRODUCTIVE CHAIN

The main concern with the use of secondary raw materials and of derived fuels of industrial residues is the incorporation of heavy metals in the clinker and their effects on the cement performance. These effects depend on the type of metals contained in the raw material and in the fuel, on their concentration level and on the kiln operation condition.

Different types of industrial residues have been used in the cement production as substitutes of the raw materials or as substitutes of the traditional fuels.

According to the European Association of Cement (CEMBUREAU, 1999), those materials whose densities are larger than the one of the titanium ( $4.51 \text{ g/cm}^3$ ) are considered heavy metals. Heavy metals are found in small amounts in the fuels used in the cement industry (coal, petroleum coke, oil or residues of fuels) and in the raw materials (limestone, clay and sand). Some of these metals, such as iron and aluminum, are essential components of cement. It is worth mentioning that not all heavy metals have harmful effects on clinker or health. As the metals cannot be destroyed, the co-processing treats them efficiently in three ways:

- The first and more important is the calculation of the feeding rate of the residues to the kiln, in order to keep the emissions below the established limits of environmental legislation.
- Second, the particulate material (CKD. cement kiln dust) kept in the cooling tower is removed from the gaseous current, and through a closed circuit it is returned to the kiln of clinker production.
- Third, the particulate material (CKD) of finer granulometry is captured by modern and efficient equipments, as electrostatic precipitators, bag filters among others, being that a really very small amount is emitted. This amount is below the established limits established by the environmental legislation. This retained material is also returned to the cement kiln, as shown in Fig. 1.

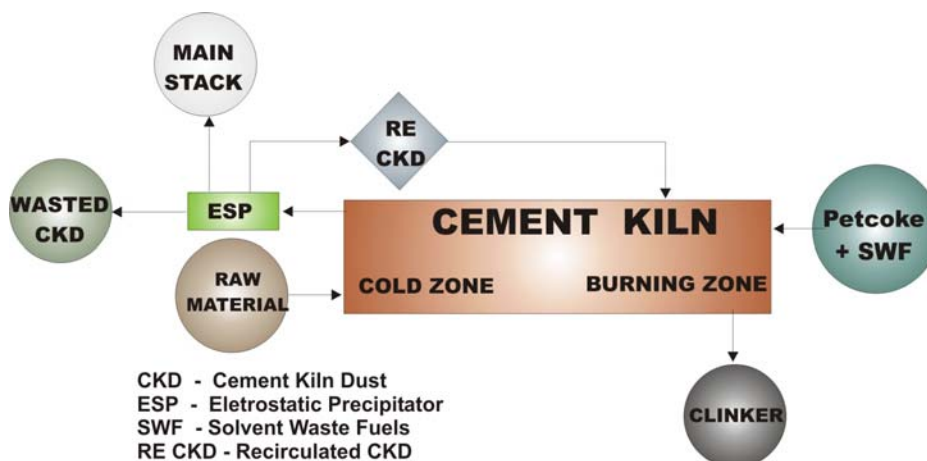


Figure 1. Cycle of heavy metals in the clinker production process.

The metals are incorporated to the cement in the following way: the raw materials, traditional fuels and the industrial residues used as fuels in the production of the cement contain organic and inorganic composite materials (heavy metals). Due to its high temperature (of the order from 1673 to 1773K), the kiln destroys the organic part, leaving the metallic compounds. The metallic compounds react chemically with the clay, the limestone and with other raw materials, forming a quite resistant crystalline structure. The metals are then permanently confined to that structure, becoming part of the clinker. The heavy metals that are controlled by the legislation are: Antimony, Arsenic, Barium, Beryllium, Cadmium, Chrome, Lead, Mercury, Silver and Thallium.

Due to toxicity of the hazardous residues, it is necessary to establish standards for the possible emissions of contaminants present in the residues during their destruction. In the Best Available Techniques - BAT, document published by the European Cement Association (IPCC, 2000), there is a classification of metals in function of their toxicity and possible adverse effects to the health human as follows.

- Class I: Cadmium (Cd), Mercury (Hg), Thallium (Tl);
- Class II: Arsenic (As), Cobalto (Co), Nickel (Ni), Selenium (Se), Tellurium (Te);
- Class III: Lead (Pb), Chromium (Cr), Copper (Cu), Vanadium (V), Tin (Sn), Antimony (Sb).

The most concerning metals are those that, for their toxicity, may cause carcinogenic infirmity, damages to different organs as liver, kidney and the nervous system and immunological problems.

Regarding the behavior of the heavy metals in the cement kiln, three classes can be classified:

- Non-volatile metals (As, Be, Co, Cr, Cu, Mn, Mo, Sb, Se, Te, V, Zn): these metals when in the presence of raw material or fuel are all incorporated to the clinker. Practically, emissions do not appear in the exhaustion gases.

European Cement Association (CEMBUREAU, 1999) adopts that the sum of the emissions of all non-volatile metals should be smaller than 0.1% of the correspondent metals at the entrance of the cement kiln.

- Semi-volatile metals (Cd, Pb): parts of these metals are volatilized due to high temperature in the zone of clinkerization in the cement kiln to soon condense in entrance zone (colder zone) of the kiln, reentering with the raw material, accomplishing a cyclical process inside of the kiln. Most of the Cadmium and Lead is incorporated in the clinker and the part that it is not condensed goes with the particulate material (CKD cement kiln dust) being captured by the filters in the exit of the gases in the stack.
- Volatile metals: like Mercury and Thallium; they are the metals with larger volatility easiness and condensation. These condense in the particles of the raw material at low temperatures (Thallium the approximately 573 - 623K, Mercury among 393 - 423 K). While Thallium is almost completely precipitate with the particulate material (CKD), only a part of Mercury is collected in the system of filters, being that the remaining part is emitted in the steam form with exhaustion gases. This process is carried out by controlling the Mercury entrance in the raw material and in the fuel.

The potential risks of the emissions of metals to the health of the population that live nearby and to the environment may indeed decrease with burning of residues, because the license for the co-processing of residues establishes more rigorous emission patterns than the established ones for the industry that just use traditional inputs.

## 5. STUDY OF THE VIABILITY OF THE LEVEL SUBSTITUTION PETROLEUM COKE FOR FUEL DERIVED FROM RESIDUES IN KILN OF CLINKER PRODUCTION

In this work, the percentage of substitution of the petroleum coke for the co-processing of a consisting residue of solvent is evaluated from ethanol with traces of heavy metal in order to support the energy demand of the process of clinker production. This is done by evaluating the possible impact of this substitution in the heavy metal emissions in the burning process of these mixtures. Simulations of petroleum coke substitution had been made for the residue of solvent in the ratio of 10%, 20%, 30% and 40%. Hence, it was calculated through a material balance, the possible heavy metal emissions of the exhausted gases flow in the kiln clinker production process. The chemical compositions of the petroleum coke and solvent residue used in the calculations are presented in Tab. 2 and 3 respectively.

### 5.1. Calculation of the combustion gases outflow for a dry way process

In order to analyze the level of concentration of the metal emissions in the stack, it was necessary to obtain the volumes of gases generated in the combustion of fuels. It is carried out a simulation of a constituted mixture of fuels of petroleum coke and residue of solvent to assist an energy consumption of 3600 kJ/kg in a system of kiln with cyclones preheater, whose schematical representation is presented in Fig. 2. For a production of 3000 tons/day or approximately 34.72 kg/s of clinker, using Eq. (1), Eq. (2) and Eq. (3), the specific consumption of thermal energy for each fuel of the simulation and its consumption in the process of burning in mass and molar flow was calculated. Then, it is mounted reaction of stoichiometric combustion of the burning of these fuels, for the kiln already mentioned, as well as the reaction of combustion with 3% of free O<sub>2</sub>. Being obtained finally for Eq.(4), the flow of exhausted gases in the stack of the kiln correct normal conditions of temperature and pressure, whose values are presented afterwards in the sub-item resulted in Fig. 3.

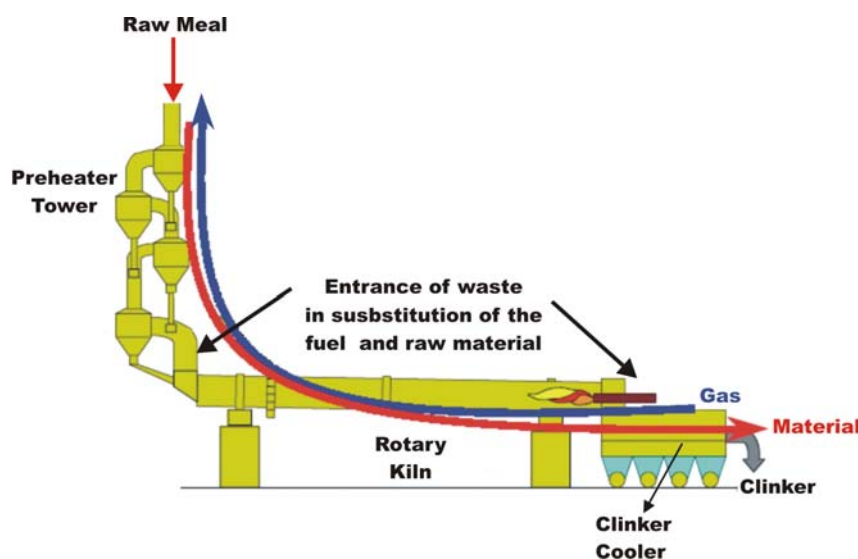


Figure 2. Kiln system with preheater co-processing residues (Oliveira, 2006)

$$CEE_{Combust.} = CEE \cdot \%Combust \quad (1)$$

Where:

$CEE_{combust}$  - Specific consumption of thermal energy for the fuel [kJ/kg clinker]

$CEE$  - Specific consumption of total thermal energy for the process [kJ/kg clinker]

$\% Combust$  - Percentile of fuel

### 5.1.1. Calculation of fuel consumption ( $Q_{tdcomb}$ )

$$Q_{tdcomb} = \frac{Production_{clinker} \cdot CEE_{Combust.}}{PCI} \quad (2)$$

Where:

$Q_{tdcomb}$  - Mass flow of fuel consumption [kg/s]

$Production_{clinker}$  - Clinker Production in the burning process [kg/s]

$PCI$  - Lower Calorific Value [kJ/kg]

### 5.1.2. Calculation of the molar flow fuel

$$N_{mol} = \frac{Q_{tdcomb} \cdot \% element}{MM_{element}} \quad (3)$$

Where:

$N_{mol}$  - Molar flow of fuel consumption [kmol/s]

$\% element$  - Percentile in weight of the chemical species contained in the fuel

$MM_{element}$  - Molar mass of the chemical species contained in the fuel [kg/kmol]

### 5.1.3. Calculation of the combustion gases flow ( $V_{gc}$ )

With the calculations accomplished previously are obtained for Eq. (4) the gases flow that is emitted during the combustion process in clinker production kiln, considering the water steam (wet base) and dry base.

$$V_{gc} = \frac{R \cdot T \cdot \dot{V}_{gc}}{Pa} \quad (4)$$

Where:

$\dot{V}_{gc}$  - Gases mass flow, product of the combustion (dry base) [kmol/s]

$R$  - Constant universal of the gases 8.314 [kJ/kmol K]

$T$  - Absolute temperature [K]

$Pa$  - Atmospheric pressure 101.325 [kPa]

### 5.2. Calculation of the heavy metals concentration in fuel

Once the flow of the combustion gases is calculated, the concentration of the heavy metals in the fuel is obtained using Eq. (5). Then, the amount of heavy metal incorporated to clinker according the retention percentile given by Kleppinger (1993) and Carpio (2005), from where studies accomplished by Seebach and Tompkins (1990) and Roth (1992) are extracted and presented in Tab. 4. Finally, through a mass balance of heavy metals in the process, the concentrations of heavy metals in the exhausted gases are calculated.

$$Q_{metal} = \left( \frac{\% metal_{Combust}}{100} \right) \cdot Q_{tdcomb} \quad (5)$$

Where:

$Q_{metal}$  - Mass metal flow in the fuel (kg/s)

$\% metal_{Combust}$  - Percentile in weight of metal in the fuel

The calculated concentrations will be compared with the constant emission patterns in the CONAMA Resolution 264 from 26/08/99 that establishes at national level, the emission maximum limits of heavy metals for the activity of co-processing of residues in rotary kilns of clinker production, which are presented in Tab.5.

Table 4. Retention percentage of heavy metals in the clinker and CKD (Kleppinger, 1993 and Carpio, 2005).

| Metal <sup>1</sup> | Seebach and           | Roth  |
|--------------------|-----------------------|-------|
| Antimony           | $\geq 99.77 \pm 0.08$ | 99.89 |
| Arsenic            | $\geq 99.89 \pm 0.29$ | 99.91 |
| Barium             | $\geq 99.88 \pm 0.29$ | 99.97 |
| Beryllium          | $\geq 99.87 \pm 1.33$ | 99.99 |
| Cadmium            | $\geq 99.56 \pm 0.44$ | 99.88 |
| Chromium           | $99.86 \pm 0.40$      | 99.97 |
| Lead               | $99.85 \pm 0.20$      | 99.91 |
| Mercury            | $\geq 61.3 \pm 32.5$  | 88.39 |
| Nickel             | $\geq 99.96 \pm 0.01$ | 99.93 |
| Selenium           | $\geq 95.40 \pm 1.78$ | 92.56 |
| Silver             | $\geq 99.84 \pm 0.18$ | 99.96 |
| Thallium           | $90.12 \pm 10.71$     | 99.80 |
| Vanadium           | $\geq 99.99 \pm 0.00$ | 88.37 |
| Zinc               | $99.79 \pm 0.26$      | 99.97 |

<sup>1</sup> for the other metals that don't consist of this table were adopted in this work a percentile of 99% of retention in the clinker.

Table 5 Emissions maximum limits

| Pollutant                                | Emissions maximum limits  |
|--|---|
| Mercury (Hg)                             | 0.05 mg/Nm <sup>3</sup> corrected 7% of O <sub>2</sub> (dry base) |
| Lead (Pb)                                | 0.35 mg/Nm <sup>3</sup> corrected 7% of O <sub>2</sub> (dry base) |
| Cadmium (Cd)                             | 0.10 mg/Nm <sup>3</sup> corrected 7% of O <sub>2</sub> (dry base) |
| Thallium (Tl)                            | 0.10 mg/Nm <sup>3</sup> corrected 7% of O <sub>2</sub> (dry base) |
| As+Be+Co+Ni+Se+Te                        | 1.40 mg/Nm <sup>3</sup> corrected 7% of O <sub>2</sub> (dry base) |
| AS+Be+Co+Cr+Cu+Mn+Ni+Pb+Sb+ Se+Sn+Te +Zn | 7.00 mg/Nm <sup>3</sup> corrected 7% of O <sub>2</sub> (dry base) |

Source: CONAMA (1999)

## 6. CALCULATION OF ADIABATIC FLAME TEMPERATURE

The values for the adiabatic flame temperature were obtained applying Eq. (6) (Van Wylen and Sontag, 2003):

$$H_r = H_p \quad (6)$$

Where:

$$H_r = \sum_r n_e \cdot (h_f^0 + \Delta h)_e \quad (7)$$

$$H_p = \sum_p n_s \cdot (h_f^0 + \Delta h)_s \quad (8)$$

$H_r$  and  $H_p$  refer to the reagents and products enthalpies respectively,  $n_e$  and  $n_s$  the kmol number of each reagents and products compounds.

## 7. CALCULATION OF TIME RESIDENCE OF THE GASES IN ROTARY KILN

Taking into account the characteristics of the rotary kiln in Tab. (6) and using Eq. (9), the residence time of gases in the kiln may be calculated and they are shown in Tab. (7).

$$t_R = \frac{\pi \cdot L \cdot D^2}{4 \cdot V_g} \quad (9)$$

Where:

$t_R$  - Time residence of the gases [s]

$L$  - Kiln length [m]

$D$  - Internal diameter of kiln [m]

$V_g$  - Volumetric flow of gases [m<sup>3</sup>/s]

Table 6. Characteristics of the rotary kiln

| Characteristics of the rotary kiln | Units           |              |
|------------------------------------|-----------------|--------------|
| Specific energy consumption        | kJ/kg           | 3600         |
| Clinker production                 | Kg/s (tons/day) | 34.72 (3000) |
| Flame temperature in rotary kiln   | K               | 2273.15      |
| Temperature in kiln exit           | K               | 1473.15      |
| Kiln length                        | m               | 68           |
| Inside diameter of the kiln        | m               | 4            |

Source: Mujumdar *et al* (2006)

## 8. RESULTS AND DISCUSSION

The main results obtained in this work are presented in the following figures. Tab. 7 supplies the average gas residence time in the rotary kiln in function of the energetic substitution of the solvent residue.

Table 7. Average gas residence time in the rotary kiln of clinker production

| Energetic substitution of the solvent residue in (%) | Average gas residence time (s) |
|--|--------------------------------|
| 10   | 1.519                          |
| 20   | 1.494                          |
| 30   | 1.469                          |
| 40   | 1.446                          |

The mass flow of consumption of fuel in the percentage levels of energy substitution proposed in this work is presented in Fig. 3.

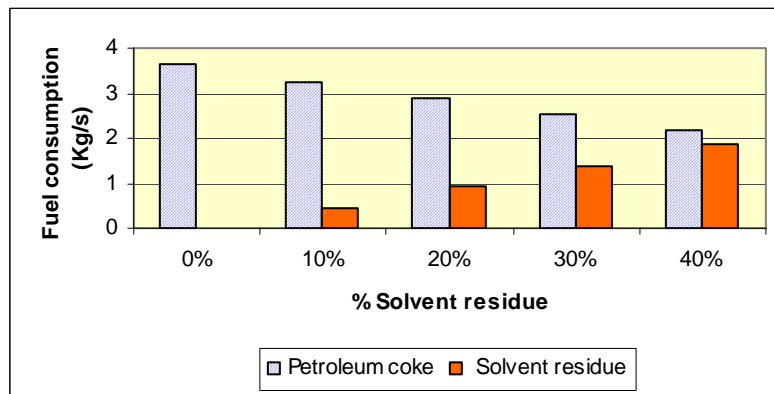


Figure 3. Fuel consumption in function of the percentage of residues in the burning process.



The volumetric flow of gases calculated at the exit of the stack with 3% of free O<sub>2</sub> (dry base) and the adiabatic flame temperature in function of the percentage of energy substitution of the petroleum coke for the solvent residue are presented in Tab. 8.

Table 8. The volumetric flow calculated of the gases in the stack exit 3% free O<sub>2</sub> (dry base) and the adiabatic flame temperature in function of the percentage of energy substitution of petroleum coke for the solvent residue.

| Energetic substitution of solvent residue in (%) | V (Nm <sup>3</sup> /s) 3% free O <sub>2</sub> (dry base) | Adiabatic flame temperature (K) |
|--|--|---------------------------------|
| 10   | 47.79  | 2243                            |
| 20   | 48.03  | 2260                            |
| 30   | 48.26  | 2276                            |
| 40   | 48.49  | 2292                            |

In Fig. 4 are presented the emissions estimates of heavy metals thrown in the atmosphere corrected to 7% of O<sub>2</sub> (dry base), comparing with the maximum emission limits according to the Resolution 264 of CONAMA (1999).

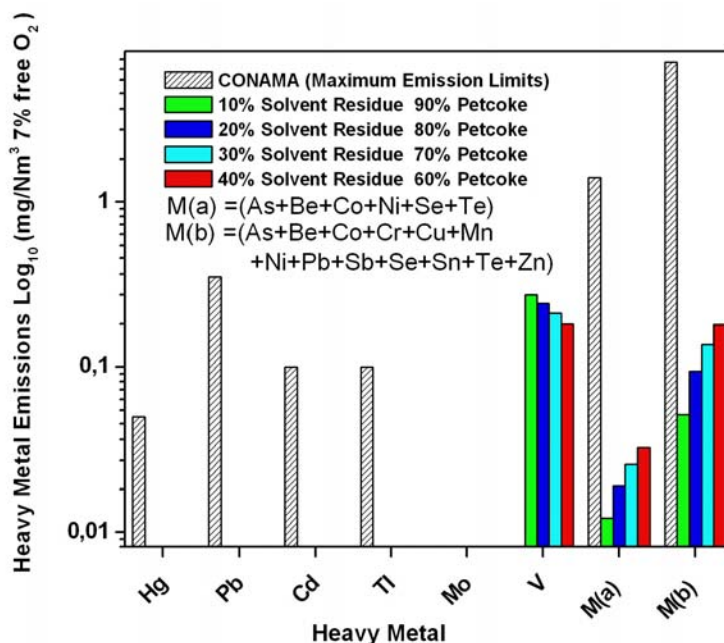


Figure 4. Emissions at the exit of the stack of metals heavy corrected to 7% of free O<sub>2</sub> compared with the standards emission of the CONAMA

The technology of secondary fuel burning and co-processing of residues is considered an efficient form for the final destination of some types of industrial residues, mainly those that possess some calorific value. The burning of secondary fuels and residues in rotary kilns of clinker production in the manufacture of the cement has favorable particular characteristics, such as: the high temperature of the kiln (around 2273 K); the elevated time of residence of the combustion gases, which can reach 6 seconds during the total course; the alkalinity of the atmosphere that contributes to neutralize the action of acid gases (as HCl) as well as the sulfur that can react and leave the kiln under the form of sulfates; the lack of generation of solid residues, since the dust of the cement kiln (CKD) can be re-fed in the kiln, and the incorporation of the ashes to the clinker that promotes the immobilization of heavy metals. All this is considered as being an important factor for the effective destruction of industrial residues, not only in the form of fuels, but also in the form of raw material in the clinker kilns. However, special cares should be observed regarding the use of secondary raw materials and of derived fuels of industrial residues, mainly in what regards the incorporation of element traces in the clinker and their effects in the cement performance. It is known, for instance, that the presence of heavy metals influences the process of hydration of the cement pastes in bigger or smaller degrees. However, in spite of the incorporation of metals to the clinker in considerable levels in some cases, due to the toxicity of some elements contained in the residues, the need of limiting the substitution of the traditional fuels exists, because many more volatile heavy metals introduced in the kiln through the residues or secondary fuels can be emitted to atmosphere in

concentrations of the order of  $\mu\text{g}/\text{Nm}^3$ . It is like this, there is a limit to its introduction for the feeding rate, being controlled by this way the emissions of non-incorporated elements that are susceptible to be emitted by the stack, together with the exhaustion gases.

## 9. CONCLUSION

The use of alternative fuels has enabled the technological development of the process, through improvements in the preheating equipments, in cooling and burning, besides new types of refractory that reduces even more the heat losses from the kiln walls and support the aggression of smaller components originating from the burning of alternative fuels. Hence, the use of traditional or alternative fuels in the clinker production is controlled by their policy of energy use, prices, operational order restrictions, availability and maximum levels of pollutant emission originating from their burning.

With base on the degree of substitution of the main fuel (petroleum coke) by the alternative fuel (residue of solvent studied in this work) it can be conclude that there would not be problems in relation to the established limits for all of the concentrations of heavy metals in the levels of substitution from 10% to 40% involved in the study. By analyzing the emission estimates for a substitution of the order of 40%, the sum of the emissions of the controlled metals (Co+Cu+Mn+Ni+Zn) totaled about  $0.180 \text{ mg}/\text{Nm}^3$ . Therefore, the concentrations are well below the acceptable maximum limit of  $7.0 \text{ mg}/\text{Nm}^3$ . However, it is worth mentioning that this result is specific for the case studied. Hence, the results must not be generalized, even if there is chemical similarity in fuels compositions that will be burned.

## 10. ACKNOWLEDGMENT

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