ANALYSIS OF THE FEASIBILITY OF COPROCESSING OF INDUSTRIAL WASTES IN CEMENT KILNS THROUGH COMPUTATIONAL MODEL FOR DETERMINING THERMAL PARAMETERS

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Abstract. *This work presents a computational method developed in FORTRAN language for the determination of thermal parameters necessary for the evaluation of the thermal destruction efficiency of hazardous substances present in industrial waste in the activity of coprocessing in rotary kilns of cement factories. Solid wastes as used tires, oily, petrochemical and chemical wastes, among others, are thermally destroyed, taking advantage of their calorific value in the process, and its ashes incorporated into the clinker. For the determination of parameters such as flame temperature, residence time, gas volume, average flow rates and velocities, a computational model was constructed, tested with the operational data of a clinker production facility. The flame temperatures are calculated in the firing region of the kiln and inside the precalciner, taking into account the feed rates of the raw mix and their composition, besides the reaction heats in the formation of clinker compounds and the necessary heat for the heating of the solids up to the reaction temperatures. Finally, through an estimate for the temperature inside the rotary kiln, one can evaluate whether a particular undesirable component contained in an industrial waste can be destroyed or not in the kiln or precalciner by using the Arrhenius Equation.*

Keywords: *Industrial wastes, cement kiln, computational model, thermal parameters, clinker production.*

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1 INTRODUCTION

The production of Portland cement, the main constituent of concrete, has been growing every year in the world, having doubled in the last fifteen years. This phenomenon is due to the population increase and greater investments in infrastructure in different countries. Among the largest cement producers are China, India, the European Union, the United States and Brazil. In 2015 alone, Brazil was responsible for the production of approximately 65 million tons.

Portland cement is a material obtained from the mixture of clinker, gypsum and active additives in quantities that depend on the type of application and the characteristics desired for the cement. Its main component, the clinker, is obtained by milling and homogenizing a pulverized mixture of limestone, sand, clay and iron ore, called raw mix, and subsequent burning of fuels at temperatures close to 2000 °C, so that the clinker can be formed at temperatures in the order of 1450 °C.

The raw mix is basically composed of four oxides: calcium oxide (CaO), silicon dioxide or silica (SiO_2), aluminum oxide or alumina (Al_2O_3) and iron oxide (Fe_2O_3). In the conventional notation of cement chemistry, these components are represented respectively by C, S, A and F. Close to 1450 °C, these oxides react with each other to form the main clinker compounds, namely: dicalcium silicate (C_2S), tricalcium silicate (C_3S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). However, with the oxides needed for the formation of the clinker, other substances can be found in lesser amounts in the raw material, such as MgO, SO_3, H_2O, K_2O and Na_2O.

The cement manufacturing process consists of several stages, which can be carried out either wet or dry. In the wet process units, the raw material is ground together with water, being leaded to the kiln in the form of mud or paste. In the dry process kilns, water is not used in the milling and homogenization of the raw materials, and these arrive at the kiln in the form of a fine powder called raw mix, with a maximum of 1% moisture.

The production begins with the extraction of raw materials for raw mix preparation. After being extracted, the limestone is transported to the crusher, where it passes through two stages until its size is reduced, and then stored in open air piles or silos. During storage, the limestone undergoes a pre-homogenization process. The clay, as well as the limestone, is crushed and pre-homogenized during storage. When they are removed from their deposits, they undergo a second pre-homogenization, and then are dosed and weighed with sand and iron ore, based on pre-established chemical parameters, so-called chemical modules. In sequence, the mixture is sent to the milling sector, where it passes through mills, forming very fine granules. Once it reaches the desired size, the raw mix is brought to a homogenizing silo. The homogenized raw mix is then withdrawn from the silos and transported to the preheating and precalcination tower. The raw mix is inserted in the superior part of the cyclones tower and goes down by its stages, finding in its way the hot gases from the kiln. Due to the heat exchange between these gases and the solids in suspension, occurs the evaporation of moisture that may still be in the mix and begins the decarbonization reaction of magnesium carbonate ($MgCO_3$). With the increase of temperature in the last stages and precalciner, occurs the calcination of calcium carbonate ($CaCO_3$), which dissociates to form calcium oxide (CaO) and carbon dioxide (CO_2). This reaction consumes more than half of all the heat

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needed to the process. Therefore, precalciners were inserted into the system. In addition to being a combustion chamber that can burn up to 60% of the fuel required for the process, the precalciner provides the energy required for the raw material to enter the rotary kiln almost fully calcined.

After passing through the precalciner, the mixture enters the rotary kiln, a cylindrical steel tube, internally coated with refractory bricks, which serve to protect the steel casing from high temperatures and also reduce heat loss to the outside. This kiln is slightly inclined to the horizontal plane, of the order of 3%, and rotates slowly, with rotations between 2 and 4 rpm. The mixture enters through its upper end and moves by the action of gravity and rotation of the kiln to the outlet end, where the main burner is located.

The raw mix, when moving inside the kiln, is gradually heated to about 1450 °C by the combustion gases exiting the burner towards the upper end of the kiln. As the temperature increases, the chemical reactions that originate the clinker, which is formed by four main compounds, occur.

After passing through the kiln, the clinker undergoes a sudden cooling. This should be done so that the clinker has its chemical and crystalline characteristics stabilized, as well as facilitating its handling and transportation until the next steps of the process. The most common types of coolers are the drum, the satellites and the grill ones, but for kilns with precalciners, the grill cooler is the most suitable. In this cooler, the air is blown through the grilles, coming from compartments beneath them. The air, after being heated by the heat exchanges with the clinker, is called secondary air and is used for combustion in the main burner. However, the amount of air employed is greater than needed for that burner. Then, the air in excess is used as tertiary air for combustion in the precalciner. This process improves the thermal efficiency of the system, since it partially recovers the enthalpy contained in the clinker when leaving the kiln.

In the stage after cooling, the clinker is sent to a silo where it is stored for a time and then sent to a ball mill or a roller mill where it is milled with gypsum to form the most commonly used Portland cement. Adding active additives to the mill, such as blast furnace slag, pozzolan materials, ashes, and other materials, can produce other types of cement, for more specific applications. After reaching the specified granulometry, the different types of cement are stored in silos separately, being stored until the moment of the expedition. They can be supplied in bulk or in 50 kg bags.

The cement industry is also one of the largest energy consumers in the world, either thermal or electric. In these industries, a large amount of energy is used to dry the raw materials and also to maintain the high temperatures they need to reach inside the kilns to perform clinker formation reactions, as well as the energy for cooling the clinker and the energy used for the operation of equipment and machinery at all stages of production.

The conventional fuels used are coal, charcoal, fuel oil and natural gas. However, several researches in the last decades have been dedicated to the study of the use of alternative fuels in the cement industries, as residues and byproducts of other industrial sectors. The charcoal fines, which are the refuse of charcoal used in siderurgy, petroleum coke, which is a byproduct of the cracking process in oil refineries, used tires, urban waste and agricultural waste are examples of alternative fuels currently used in the manufacture of cement. Even hazardous wastes have been used as fuel since the high operating temperatures of the kiln

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ensure the destruction of most harmful substances to human health, being even more efficient than incinerators.

According to Silva (1994), fuels used in cement plants must, in addition to being economically feasible, have physico-chemical characteristics compatible with the requirements of the combustion process in the rotary kiln and precalciner, such as: lower heating value (LHV) of at least 8370 kJ/kg (2000 kcal/kg), in order to obtain a minimum temperature in the sintering zone; have chemical components which have little or no negative influence on the final composition of the clinker and its quality from the products formed during combustion; and the possibility of generating a characteristic type of flame, which varies according to the type of fuel.

In this way, the present work has the objective of evaluating the feasibility of coprocessing of industrial waste in cement plants, through computational simulations and analysis from the economic and environmental points of view. The method used considers a dry process cement plant containing precalciner and a 4-stage preheater, and consists of obtaining the combustion balanced equations as well as the adiabatic and real flame temperatures from the First Law of Thermodynamics for a control volume in the flame region.

Simulating different mixtures of fuels, one can analyze the generation of pollutants emitted from the gas flows at the exit of the precalciner by the combustion equations. By calculating the flame temperature, one can also simulate the effect that the addition of mineralizing substances to the solid material would cause in the clinker produced, with the main objective of reducing the amount of fuel used. Finally, by an estimate of the temperatures inside the rotary kiln through the flame temperature, one can evaluate if a certain undesirable component contained in the residue is destroyed or not inside the oven using the Arrhenius equation.

2 OBTAINMENT OF THE COMBUSTION CHEMICAL EQUATIONS

The first step is to obtain the thermal energy per unit of time required to manufacture the clinker, multiplying the mass flow of clinker produced by the required energy, as shown in Equation (2.1). The calcination reaction consumes about 60% of the total energy of the process. In dry process plants with preheating tower and precalciner, it is desired that the raw mix enters the kiln with calcination above 90%, which guarantees a temperature stability at the entrance of the kiln. Thus, about 60% of the total energy required in the process will be supplied in the precalciner to allow the calcination reaction to take place, and the remaining 40% of the thermal energy will be supplied by burning the fuel in the main burner of the rotary kiln, as shown in Equations (2.2) and (2.3).

$$\dot{Q}_{plant} = \dot{m}_{clinker} \cdot q_{clinker} \tag{2.1}$$

$$\dot{Q}_{kiln} = \dot{Q}_{plant} \cdot \%_{kiln} \tag{2.2}$$

$$\dot{Q}_{pcal} = \dot{Q}_{plant} \cdot \%_{pcal} \tag{2.3}$$

being: $\dot{m}_{clinker}$ the mass flow of clinker produced; $q_{clinker}$ the energy required to produce 1 kg of clinker, varying from process to process; $\dot{Q}_{plant}$ the total energy required in the plant; $\dot{Q}_{kiln}$ the energy required in the rotary kiln; $\dot{Q}_{pcal}$ the energy required in the precalciner; and $\%_{kiln}$ and $\%_{pcal}$ the percentage of the total energy of the plant destined to the kiln and to the precalciner, respectively.

With the information of the energy required for the burners of the installation, as well as which fuels will be used, their respective heating values and the percentages in which they will be used, one can estimate the mass flow rate of each of them, according to Equations (2.4) and (2.5).

$$\dot{m}_{f_{kiln}} = \frac{\dot{Q}_{kiln} \cdot \%_f}{LHV_f} \tag{2.4}$$

$$\dot{m}_{f_{pcal}} = \frac{\dot{Q}_{pcal} \cdot \%_f}{LHV_f} \tag{2.5}$$

being: $\dot{m}_{f_{kiln}}$ and $\dot{m}_{f_{pcal}}$ the mass flow of a given fuel in the kiln and precalciner, respectively; $\%_f$ the percentage of the analyzed fuel in the corresponding mix; and LHV_f its lower calorific value.

The molar flows of each chemical compound present in the fuels, such as carbon, hydrogen, sulfur, nitrogen, oxygen and water, can be determined taking into account their molar mass and their percentage presence in the chemical composition of each fuel, according to the Equation (2.6).

$$\dot{n}_{comp} = \frac{\dot{m}_f \cdot \%_{comp}}{M_{comp}} \tag{2.6}$$

being: $\dot{n}_{comp}$ the molar flow of a given compound; $\dot{m}_f$ the mass flow of the analyzed fuel; $\%_{comp}$ the mass percentage of the compound in the fuel; and M_{comp} the molar mass of the compound.

Adding up the molar flows for each chemical compound calculated previously and considering that all carbon, hydrogen and sulfur react with oxygen forming carbon dioxide, water and sulfur dioxide, and that the nitrogen remains inert, the combustion chemical equation can be balanced and the amount of air to be injected into the burner determined.

In the products of the reaction, the carbon dioxide from the calcination reaction is also added. To ensure a more complete combustion, the burners are usually operated with a small excess of air. This excess should not be too high as it absorbs some of the heat intended for the clinker formation chemical reactions. The molar flow of free oxygen can be calculated by the excess of air, as shown in Equation (2.7).

$$\frac{\%O_{2\,\mathrm{free}}}{100\%} = \frac{\dot{n}_{O_{2\,\mathrm{free}}}}{\left(\dot{n}_{\mathrm{total}} - \dot{n}_{H_2O}\right) + 4{,}76\,\dot{n}_{O_{2\,\mathrm{free}}}} \tag{2.7}$$

In the combustion reaction to the precalciner, the products of combustion and the carbon dioxide from calcination in the kiln enter as reactants in the precalciner, with only oxygen reacting and the other compounds remaining in the products.

3 FLAME TEMPERATURES

According to Çengel and Boles (2011), the adiabatic flame temperature is the maximum temperature reached by the products of combustion during burning, which occurs only when there is no heat loss to the neighborhood of the flame, that is, when the process occurs adiabatically. Equation (3.1) presents one of the mathematical forms of the First Law of Thermodynamics for a control volume with an input and an output.

$$\dot{Q} + \left(h_1 + \frac{{V_1}^2}{2} + gz_1\right)\dot{m}_1 = \left(h_2 + \frac{{V_2}^2}{2} + gz_2\right)\dot{m}_2 + \dot{W}_{\mathrm{shaft}}$$

By the principle of mass conservation, we have that $\dot{m}_1 = \dot{m}_2$. Considering that the reactants enter this imaginary control volume by its single input, they suffer complete combustion inside it and leave it by its single outlet, that there is no work being done and neglecting the variations of kinetic and potential energy, there is for the adiabatic case that the total enthalpies of the reactants and of the products must be equal, according to Equation (3.2).

$$H_{\mathrm{reactants}} = H_{\mathrm{products}} \tag{3.2}$$

In molar terms, Equation (3.2) can be rewritten as Equation (3.3) for the cases in which the fuel is burnt pulverized.

$$\sum_{\mathrm{fuels}} \dot{m}\,(\mathrm{LHV}) + \sum_{\mathrm{gases}} \dot{n}(h - h_0) = \sum_{\mathrm{prod}} \dot{n}(h - h_0) \tag{3.3}$$

The term corresponding to the reactant gases comprises the primary and secondary combustion air in the kiln and, in the case of the precalciner, the tertiary air and the gases coming from the kiln. As the enthalpies are temperature dependent, the adiabatic flame temperature can be found by an iterative method. However, to avoid the use of tables and to

facilitate computational implementation, empirical formulas for heat capacities at constant pressure are used to calculate the enthalpies of different substances, as can be observed in Equations (3.4) and (3.5).

$$c_p = a + bT + cT^2 + dT^3 \tag{3.4}$$

$$h - h_0 = \int_{T_0}^{T} c_p dT = a(T - T_0) + \frac{b}{2}\left(T^2 - {T_0}^2\right) + \frac{c}{3}\left(T^3 - {T_0}^3\right) + \frac{d}{4}\left(T^4 - {T_0}^4\right) \tag{3.5}$$

The molar flows of each chemical are obtained from the combustion equation. However, the equations for the heat capacity at constant pressure are shown in Table 3.1.

Table 3.1. Equations for the heat capacity at constant pressure of some gases present in the combustion reaction.

Gas	Equations for the heat capacity at constant pressure (kJ/kmol·K)	Temperature range
CO_2	$c_p = 75.464 - 1.872 \cdot 10^{-4}\, T - \frac{661.42}{\sqrt{T}}$	273 K – 3800K
H_2O	$c_p = 29.163 + 1.449 \cdot 10^{-2}\, T - 0.202 \cdot 10^{-5}\, T^2$	273 K – 3800K
SO_2	$c_p = 25.762 + 5.791 \cdot 10^{-2}\, T - 3.809 \cdot 10^{-5}\, T^2 + 8.607 \cdot 10^{-9}\, T^3$	273 K – 1800K
O_2	$c_p = 28.167 + 0.630 \cdot 10^{-2}\, T - 0.075 \cdot 10^{-5}\, T^2$	273 K – 3800K
N_2	$c_p = 27.318 + 0.623 \cdot 10^{-2}\, T - 0.095 \cdot 10^{-5}\, T^2$	273 K – 3800K

Source: Sandler (2006).

The enthalpy equations for the air should be evaluated at environment temperature or at the secondary air temperature in the kiln and at the tertiary air temperature in the precalciner. Also, the equations for the gases coming from the kiln should be evaluated at the temperature at which they enter the precalciner. The development of Equation (3.3) leads to a polynomial equation as a function of the flame temperature to be calculated. In the computational implementation, we opted for the bisection method to solve the problem.

The adiabatic flame temperature represents the maximum temperature reached by the products in an ideal combustion, but in practice there is heat exchange between the flame and its neighborhood. In the case of the precalciner and the rotary kiln, much of the heat generated is absorbed by the raw material, so that it increases its temperature and the reactions of calcination and clinkering occur. Thus, a model was developed to calculate an approximate real flame temperature, neglecting losses to the external environment, but considering the enthalpy of heating and reaction of the solids.

Table 3.2 shows the usual temperature ranges at which each of the solids chemical reactions occurs during the clinker production process.

Table 3.2. Usual temperature ranges for transformation reactions.

Temperature range	Process	Chemical reaction
400 °C a 900 °C	Clay decomposition	
600 °C a 1000 °C	Decomposition of limestone	$CaCO_3 \rightarrow CaO + CO_2$
800 °C a 1300 °C	Formation of C_2S, C_3A and C_4AF.	$2\ CaO + SiO_2 \rightarrow C_2S$
		$3\ CaO + Al_2O_3 \rightarrow C_3A$
	Formation of the liquid phase above 1250 ° C.	$4\ CaO + Al_2O_3 + Fe_2O_3 \rightarrow C_4AF$
1250 °C a 1450 °C	Formation of C_3S	$CaO + C_2S \rightarrow C_3S$
1300 °C a 1240 °C	Cooling of clinker for liquid state solidification.	
1240 °C a 100 °C	Cooling of the clinker in the cooler.	

Source: Adapted from Teka (2015).

In the preheating system, the solids are heated from the inlet temperature of 333K to 933K at the inlet of the precalciner. For the purpose of calculating the temperatures in the precalciner, it was assumed that the calcination reaction occurs at 1073K. In the kiln, the formation reactions of C_3A and C_4AF occur at 1423K, the formation reaction of C_2S occurs at 1473K and the formation reaction C_3S occurs at 1633K, the solids being heated up to 1723K. As it is assumed that the reactions occur instantly when the reactants reach the reaction temperature, the molar flow of the components of the raw mix and clinker must be updated after each reaction.

The molar flow at the inlet and outlet of the precalciner and the kiln are obtained by means of Bogue's potential calculation, described in more detail in Silva (1994), Taylor (1997) and Duarte (1999). Basically, it resumes to direct all Fe_2O_3 to C_4AF, the remainder Al_2O_3 to C_3A and distribute the remainder CaO and all SiO_2 between C_2S and C_3S by means of a system of equations.

Altering Equation (3.3) for the case of real flame, we have Equation (3.6):

$$\sum_{\text{fuels}} \dot{m}\,(\text{LHV}) + \sum_{\text{gases}} \dot{n}(h - h_0) - \sum_{\text{comp}} \dot{n}(h - h_0) - \sum_{\text{reactions}} \frac{\dot{n}}{M}\Delta H = \sum_{\text{prod}} \dot{n}(h - h_0) \tag{3.6}$$

The heats of reaction involved in the process are given in Table 3.3.

Table 3.3. Heats of reaction for calcination and clinker formation reactions at 20 °C.

Chemical reaction	Heats of reaction (kJ/kg)
$CaCO_3 \rightarrow CaO + CO_2$	1766
$MgCO_3 \rightarrow MgO + CO_2$	1188
$2\ CaO + SiO_2 \rightarrow C_2S$	-715
$CaO + C_2S \rightarrow C_3S$	-528
$CaO + Al_2O_3 \rightarrow CA$	-309
$12\ CaO + 7\ Al_2O_3 \rightarrow C_{12}A_7$	-169
$3\ CaO + Al_2O_3 \rightarrow C_3A$	-15
$4\ CaO + Al_2O_3 + Fe_2O_3 \rightarrow C_4AF$	-84

Source: Silva (1994).

The heating enthalpies can be obtained from empirical equations as a function of the initial and final temperatures, as shown in Equations (3.7) and (3.8) for the components and coefficients present in Table 3.4.

$$(h_T - h_{298}) = A \cdot T + B \cdot 10^{-3} \cdot T^2 + C \cdot 10^5 \cdot T^{-1} + D \tag{3.7}$$

$$\left(h_{T_2} - h_{T_1}\right) = A \cdot (T_2 - T_1) + B \cdot 10^{-3} \cdot \left({T_2}^2 - {T_1}^2\right) + C \cdot 10^5 \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.8}$$

4 RESIDENCE TIME AND DESTRUCTION

In the coprocessing of industrial waste in the manufacture of clinker, fuels should not be chosen only based on their energy potential, but also taking into account the chemical composition of them. The residence time of the combustion gases in the kiln and in the precalciner must be longer than the time required to completely destroy the wastes with an efficiency greater than 99%.

Considering the gases products of combustion as ideal gases, the volumetric flow of them can be calculated by Equation (4.1).

$$\dot{V}_g = \frac{\dot{n}_{total} R T}{P} \tag{4.1}$$

being: $\dot{V}_g$ the volumetric flow; $\dot{n}_{total}$ the sum of the molar flows of the gases products of combustion on a wet basis; R the universal gas constant, 8314 (J/kmol.K); T the average temperature of the gases; and P the absolute pressure within the control volume considered, generally below the atmospheric pressure.

Table 3.4. Coefficients used in heating enthalpy equations.

Compounds		A	B	C	D	Temperature range (K)
$CaCO_3$	S	24.98	2.62	6.20	-9760.0	298 – 1200
SiO_2	SA	11.22	4.10	2.70	-4615.0	298 – 848
	SB	14.41	0.97	0.00	-4455.0	848 – 2000
Al_2O_3	S	27.49	1.41	8.38	-11132.0	298 – 1800
Fe_2O_3	SA	23.49	9.30	3.55	-9021.0	298 – 950
	SB	36.00	0.00	0.00	-11980.0	950 – 1050
	SG	31.71	0.88	0.00	-8446.0	1050 – 1800
$MgCO_3$	S	18.62	6.90	4.16	-7560.0	298 – 750
SO_3	G	13.90	3.05	3.22	-5495.0	298 – 1500
Na_2O	S	15.70	2.70	0.00	-4921.0	298 – 1100
K_2O	G	16.40	0.00	0.00	0.00	298 – 5000
P_2O_5	S	16.75	54.00	0.00	-9794.0	298 – 631
	G	73.60	0.00	0.00	-6570.0	631 – 1500
CaO	S	11.67	0.54	1.56	-4051.0	298 – 2000
MgO	S	10.18	0.87	1.48	-3609.0	298 – 2100
C_2S	SB	34.87	4.87	6.26	-12929.0	298 – 970
	SA	32.16	5.51	0.00	-9814.0	970 – 1710
	SA’	49.00	0.00	0.00	-19110.0	1710 – 2000
C_3S	S	49.85	4.31	10.15	-18651.0	298 – 1800
C_3A	S	62.28	2.29	12.01	-22801.0	298 – 1800
C_4AF	S	110.07	2.49	23.18	-40814.0	298 – 5000
Cl	G	5.53	-0.08	0.23	-1719.0	298 – 5000
CO_2	G	10.57	1.05	2.06	-3936.0	298 – 2500
$CaSO_4$	S	18.52	0.02197	126800.0	0.0	273 – 1373
Na_2SO_4	S	14.97	26.45	0.00	-6815.0	298 – 514
	S	29.06	9.67	0.00	-7837.0	514 – 1157
	L	47.18	0.00	0.00	-10190.0	1157 – 2000
K_2SO_4	SA	28.77	11.90	4.26	-11064.0	298 – 856
	SB	33.60	6.70	0.00	-8747.0	856 – 1342
	L	47.80	0.00	0.00	-6680.0	1342 – 1700
Free lime	S	11.67	0.54	1.56	-4051.0	298 – 2000
$CaCl_2$	S	17.18	1.52	0.60	-5459.0	298 – 1055
	L	24.70	0.00	0.00	-4858.0	1055 – 1700

Source: Carvalho *et al.* (1977).

The volumetric flow, in practice, varies in each point of the kiln and the precalciner, since the temperature also varies point by point, as can be observed in Figure 4.1. The ideal would be to perform such calculations based on a temperature profile, however, as its measurement is complex and its estimation would involve many variables, besides a high computational cost, the average temperature calculated from the real flame temperature and the outlet temperature of the exhaust gases, for the kiln, shows itself like a good approximation.

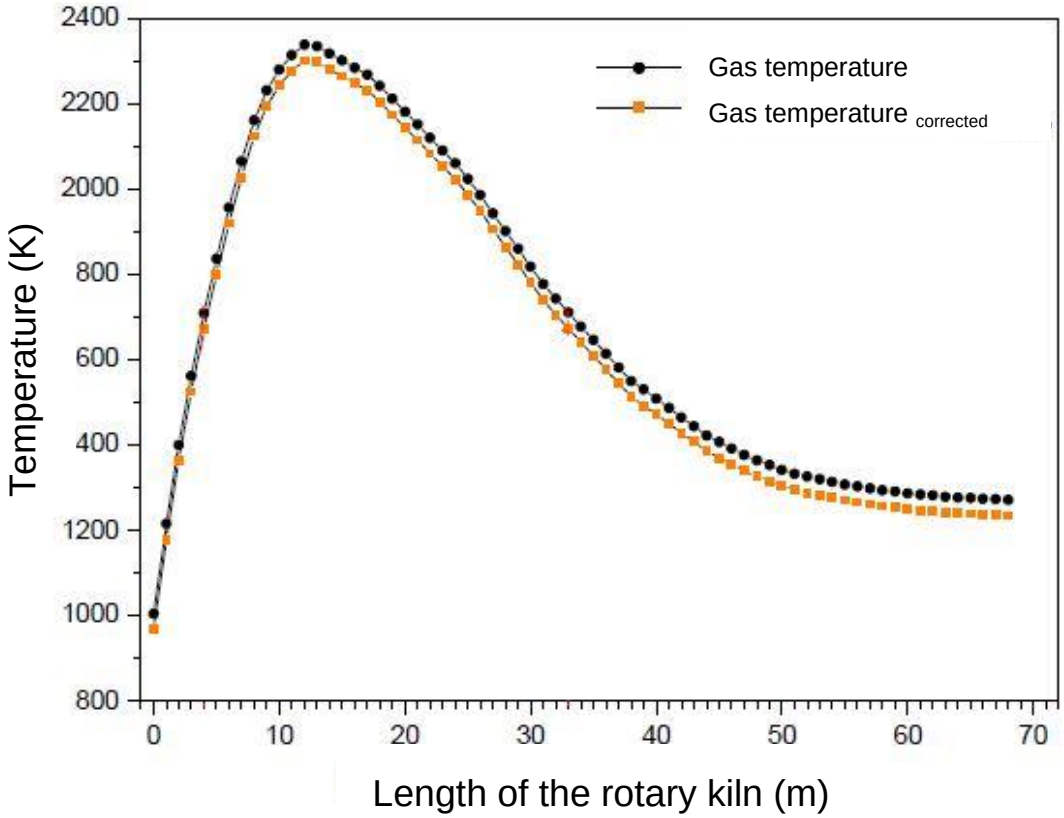

Figure 4.1. Temperature profile for a dry rotary kiln.

Source: Adapted from Score (1995) *apud* Signoretti (2008).

The gas circulation area is approximately 80% of the internal cross-sectional area of the kiln, and can be calculated by Equation (4.2).

$$A_g = 0.80 \cdot \frac{\pi {D_i}^2}{4} \tag{4.2}$$

being: A_g the circulation area of the gas and the D_i internal diameter of the control volume.

The internal diameter can be estimated from the outside diameter, discounting the thicknesses of the steel shell and the refractory bricks coating the equipment and, in the case

of the kiln, the coating thickness that forms inside. It should be noted that the thicknesses mentioned vary along the length as a function of the temperature variation.

Once the area is defined, it is possible to calculate the gases velocity in the precalciner or in the rotary kiln, as well as their residence time, by Equations (4.3) and (4.4), respectively.

$$U = \frac{\dot{V}_g}{A_g} \tag{4.3}$$

$$t_{residence} = \frac{\Delta s}{U} \tag{4.4}$$

being Δs the length covered by the gases analyzed within the control volume.

As for the time of waste destruction, this can be calculated by Equation (4.5):

$$t_{destruction} = \exp\left\{\ln\left[-\frac{1}{A}\left(\ln\frac{C_A}{C_{A_0}}\right)\right] + \frac{E_a}{RT}\right\} \tag{4.5}$$

being: A the Arrhenius pre-exponential factor, C_A the final concentration, C_{A_0} the initial concentration and E_a the activation energy, all of the compound analyzed; R the universal constant of gases; and T the average temperature of the gases.

Table 4.1 presents the values of these coefficients for some compounds that are generally found in waste destined to the coprocessing in cement plants.

5 STUDY CASE

As an application of what was seen, it was considered a dry process installation that operates with a 4-stage preheater and precalciner and produces about 3000 tons/day of clinker, employing the fuels presented in Table 5.1. The percentages in which they are used in the kiln and in the precalciner are set out in Table 5.2.

Table 4.1. Characteristics of hazardous organic compounds found in waste.

Organic Compound	Chemical formula	Kinetic Parameters (1) Pre-exponential Factor A (1/s)	Kinetic Parameters (1) Activation Energy E_a (J/kmol)	Uses and Applications (2)
Toluene	C_7H_8	$2.1 \cdot 10^{12}$	$324.5 \cdot 10^6$	Raw material from which are obtained benzene derivatives, colorants, perfumes, TNT and detergents. It is added to fuels (as an antiknocker) and as a solvent for paints.
Meta-Xylene	C_8H_{10}	$4.2 \cdot 10^{12}$	$324.4 \cdot 10^6$	Solvents and precursors of other chemicals.
Cresol	C_7H_8O	$1.0 \cdot 10^{10}$	$293.0 \cdot 10^6$	Disinfectants, dyes, insecticides.
Chlorobenzene	C_6H_5Cl	$1.9 \cdot 10^{16}$	$303.9 \cdot 10^6$	Production of herbicides, dyes and rubber.
Hexachlorobutadiene	C_4Cl_6	$2.1 \cdot 10^{12}$	$324.4 \cdot 10^6$	Solvents, algicide, herbicide.
Maleic Anhydride	$C_4H_2O_3$	$1.0 \cdot 10^{13}$	$293.0 \cdot 10^6$	Production of additives for lubricating oils; Insecticides, herbicides and fungicides.

Source: (1) Castaldini (1986) and (2) Passow (2003) *apud* Signoretti (2008).

Table 5.1. Individual elementary chemical composition of the fuels, in % of weight.

Components		Charcoal fines	Mineral coal	Imported petroleum coke	National petroleum coke	Tire scraps
Carbon	C	70.64	70.12	87.97	97.83	72.15
Hydrogen	H	3.21	4.51	3.31	036	6.74
Sulfur	S	0.29	1.28	4.69	0.96	1.23
Oxygen	O	---	1.13	0.90	---	9.67
Nitrogen	N	1.02	2.25	1.52	---	0.36
Hygroscopic water	H_2O	1.78	0.85	0.30	0.36	1.02
Ashes	ASH	23.00	19.85	1.09	0.48	8.74
Volatile	VM	22.29	33.60	11.30	8.71	67.31
LHV (kJ/kg)	LHV	21648	26928	33974	34930	32580

Table 5.2. Percentage of fuel mixtures in energy required.

Fuels	MIX in the Rotary Kiln Composition %	MIX in the Precalciner Composition %
Charcoal fines	15.0	15.0
Mineral coal	15.0	15.0
Imported petroleum coke	70.0	50.0
National petroleum coke	-	-
Tire scraps	-	20.0
Total	100.00	100.0

Table 5.3 presents some information about the studied plant and that were relevant to the combustion calculations.

Table 5.3. Data of the analyzed plant.

Total energy consumption in plant	109998.6 kJ/s
Energy consumed in the rotary kiln	40.0 %
Energy consumed in the precalciner	60.0 %
Free O_2 in the rotary kiln	1.7 %
Free O_2 in the precalciner	2.7 %
CO_2 formed in the calcination of $CaCO_3$ in the rotary kiln	0.040955 kmol/s
CO_2 formed in the calcination of $CaCO_3$ in the precalciner	0.368595 kmol/s
Percentage of secondary air	85 %
Secondary air inlet temperature in the rotary kiln	1388 K
Tertiary air inlet temperature in the precalciner	1037 K
Temperature of the exhaust gases of the rotary kiln	1473 K
Temperature of solids at the preheaters inlet	333 K
Temperature of solids at the precalciner inlet	933 K
Temperature of solids at the rotary kiln inlet	1073 K
Temperature of solids at the rotary kiln outlet	1638 K
External diameter of the rotary kiln	5 m
Rotary kiln length	70 m

By Bogue's potential calculation, the molar flows of each component of the solids are estimated from the input of the first stage of the preheater to the output of the rotary kiln, as shown in Table 5.4.

Table 5.4. Chemical composition of raw mix and clinker fluxes in kmol/s.

Compound of raw mix and clinker	Raw mix Mass Flow (kg/s)	Molar Mass (kg/kmol)	Entry of 1st Stage 60 °C	Entry of the 4th Stage and Precalciner 660 °C	Rotary kiln inlet 800°C	Rotary kiln outlet 1365°C	Clinker Mass Flow Kg/s
$CaCO_3$	40.954969	100	0.409550	0.409550	0.040955	---	---
SiO_2	6.964686	60	0.116078	0.116078	0.116078	---	---
Al_2O_3	1.873223	102	0.018365	0.018365	0.018365	---	---
Fe_2O_3	1.012847	160	0.006330	0.006330	0.006330	---	---
$MgCO_3$	1.944013	84	0.023143	0.000000	0.000000	---	---
SO_3	0.500978	80	0.006262	0.006262	0.006262	---	---
Na_2O	0.016336	62	0.000263	0000263	0.000263	---	---
K_2O	0.435633	94	0.004634	0.004634	0.004634	---	---
P_2O_5	0.070790	142	0.000498	0.000498	0.000498	---	---
CaO	---	56	---	---	0.368595	---	---
MgO	---	40	---	0.023143	0.023143	0.023143	0.925720
C_2S	---	172	---	---	---	0.009536	1.640192
C_3S	---	228	---	---	---	0.106547	24.292716
C_3A	---	270	---	---	---	0.012035	3.249351
C_4AF	---	486	---	---	---	0.006330	3.076523
Cl	0.007624	72	0.000106	0.000106	0.000106	---	---
CO_2	---	44	---	---	---	---	---
$CaSO_4$	---	136	---	---	0.003132	0.003132	0.425952
Na_2SO_4	---	142	---	---	---	0.000264	0.037488
K_2SO_4	---	174	---	---	---	0.004634	0.806316
Free lime	---	56	---	---	---	0.006200	0.347200
$CaCl_2$	---	112	---	---	---	0.001060	0.118720
Total	53.781100	---	0.585231	0.585231	0.588363	0.172881	34.920178

By inserting the data contained in the previous tables, the program implemented in FORTRAN language calculated the required mass flow of each fuel, disregarding heat losses to the environment, as shown in Table 5.5. In addition, the program provided the balanced combustion equations for the kiln and the precalciner, through which it is possible to estimate the emission of pollutant gases by the plant.

Table 5.5. Mass flows in kg/s of the fuels used in the installation.

Fuels	Precalciner	Rotary kiln
Charcoal fines	0.457311	0.304874
Mineral coal	0.367642	0.245095
Imported petroleum coke	0.971318	0.906564
Tire scraps	0.405151	-

Balanced combustion equation for the rotary kiln:

$$0.098727\ \mathrm{C} + 0.025424\ \mathrm{H_2} + 0.001454\ \mathrm{S} + 0.000342\ \mathrm{O_2} + 0.000800\ \mathrm{N_2} + 0.000568\ \mathrm{H_2O} +$$
$$+(0.112552 + 0.010453)\ \mathrm{O_2} + (0.423196 + 0.039304)\ \mathrm{N_2} \rightarrow$$
$$0.098727\ \mathrm{CO_2} + 0.025424\ \mathrm{H_2O} + 0.001454\ \mathrm{SO_2} + 0.000800\ \mathrm{N_2} + 0.000568\ \mathrm{H_2O} +$$
$$+(0.000000 + 0.010453)\ \mathrm{O_2} + (0.423196 + 0.039304)\ \mathrm{N_2} + 0.040955\ \mathrm{CO_{2_{calcination}}}$$

Balanced combustion equation for the precalciner:

$$0.139682\ \mathrm{CO_2} + 0.025992\ \mathrm{H_2O} + 0.001454\ \mathrm{SO_2} + 0.010453\ \mathrm{O_2} + 0.463299\ \mathrm{N_2} +$$
$$+0.143968\ \mathrm{C} + 0.045359\ \mathrm{H_2} + 0.001768\ \mathrm{S} + 0.001627\ \mathrm{O_2} + 0.001041\ \mathrm{N_2} + 0.001017\ \mathrm{H_2O} +$$
$$+(0.156335 + 0.052905)\ \mathrm{O_2} + (0.587821 + 0.198924)\ \mathrm{N_2} \rightarrow$$
$$0.139682\ \mathrm{CO_2} + 0.025992\ \mathrm{H_2O} + 0.001454\ \mathrm{SO_2} + 0.463299\ \mathrm{N_2} +$$
$$+0.143968\ \mathrm{CO_2} + 0.045359\ \mathrm{H_2O} + 0.001768\ \mathrm{SO_2} + 0.001041\ \mathrm{N_2} + 0.001017\ \mathrm{H_2O} +$$
$$+(0.000000 + 0.052905)\ \mathrm{O_2} + (0.587821 + 0.198924\ )\ \mathrm{N_2} + 0.368595\ \mathrm{CO_{2_{calcination}}}$$

By adding the respective molar flows of carbon dioxide and sulfur dioxide in the products of the combustion in the precalciner and multiplying by their molar masses, it is possible to obtain an estimative of the emission rate of pollutants from the plant to the atmosphere. In the analyzed case, there is an emission of 103,315.61 kg/h of CO_2 and 742.35 kg/h of SO_2, which can be compared with the environmental standards of the country where the plant is installed.

According Normative Deliberation of State Environmental Policy Council of Minas Gerais – COPAM, nº 154, August 25, 2010, the SO_2 emission limit is 280 mg/Nm ^{3} corrected to 11% O_2. For comparison with the standard, the gas composition in the system output is recalculated considering 11% free oxygen, and thus the exhaust gas flow is calculated on a dry basis, adopting a temperature of 0 °C and a pressure of 1 atm. The limit applies only to the case where the raw mix does not contribute to the emission in the form of SO_3, as the case of the analyzed plant, wherein SO_3 present in the raw mix reacts with CaO to form $CaSO_4$, the gypsum present in clinker final composition. When there is this control, the emission of SO_2 increases and other calculation procedures are prescribed in the standard.

Based on the First Law of Thermodynamics, as discussed previously, adiabatic and real flame temperatures are also calculated in both burners. These thermal parameters are contained in Table 5.6 and will be used to verify the possibility of waste coprocessing.

Table 5.6. Calculated flame temperatures.

Flame Temperatures	Precalciner	Rotary kiln
Adiabatic	2170.7 K	2945.8 K
Real	1041.0 K	2262.3 K

The flame temperatures calculation is of high importance, since they are excellent indicators of the clinker quality. In the precalciner, it must ensure that the raw mix reaches the calcination temperature and, in the rotaty kiln, must be such that the resulting temperature profile maintain the raw mix at a temperature above 1450 °C for sufficient time in order that the clinker formation reactions occur.

For the compounds presented in Table 4.1, the destruction times were calculated within the rotary kiln, according to Equation (4.5). The results are shown in Table 5.7 for an average temperature of 1867.65 K.

Table 5.7. Times of destruction for the organic waste compounds.

Organic Compound	Times of destruction (s)
Toluene	0.005224
Meta-Xylene	0.002595
Cresol	0.144287
Chlorobenzene	0.000000
Hexachlorobutadiene	0.005191
Maleic Anhydride	0.000144

To obtain the velocity of the combustion products gases in the kiln, was adopted an average temperature of 1867.65 K and an internal pressure of 1 atm or 101,350 Pa. It is also considered that the thickness of the refractory bricks varies between 4 and 8 inches and the coating thickness have about 35 cm, resulting in an internal diameter of the kiln of approximately 4 m.

$$\dot{V}_g = \frac{\dot{n}_{total} RT}{P} = \frac{0.640881 \cdot 8314 \cdot 1867.65}{101350} = 98.188 \ m^3/s$$

$$A_g = 0.80 \cdot \frac{\pi D_i}{4} = 0.80 \cdot \frac{\pi \cdot 4.0^2}{4} = 10.053 \ m^2$$

$$U = \frac{\dot{V}_g}{A_g} = \frac{98.188}{10.053} = 9.767 \text{ m/s}$$

As the average temperature adopted in a linear form does not match the actual average temperature of the kiln, it is considered, for calculation purposes, that the length the organic compounds present in the waste have to be destroyed is less than the total length of the kiln. Thus, disregarding the length of the kiln corresponding to the burner, in which the temperature drops abruptly, and the one in which occurs the reaction of calcination, where the temperature remains relatively constant, we have an "useful" length of the kiln of about 50 m. In a way, this is for safety, since if a compound is destroyed in a smaller range of the oven, he will surely be destroyed when cross it completely.

Thus, in the analyzed plant, all the six compounds in Table 5.7, if present in the waste, would be destroyed in the kiln, allowing the coprocessing of them from the environmental point of view.

6 CONCLUSIONS

In the industrial sector, the cement industry is one of the largest energy consumers in the world, either thermal or electric energy. Aiming to reduce costs, several researches in the last decades have been dedicated to the study of the use of alternative fuels in these industries, such as residues and byproducts of other industrial sectors. In order to make it feasible to use them, it must be ensured that the temperatures in the kiln are maintained high, in order to guarantee the destruction of the residues with high efficiency levels and without affecting the quality of the clinker produced.

To simulate the effects of different fuels and their quantities on clinker production, a computational method was developed and implemented in FORTRAN programming language. It allows the approximate calculation of the consumption of each fuel, either conventional or alternative, and the emission of pollutants by the plant. It also allows verifying if the time of destruction of dangerous compounds contained in coprocessed waste is compatible with the time of passage of the gases generated by the "useful" length of the kiln, adopting an average temperature from the flame temperature.

The advantage of considering an average temperature of the gases from the flame temperature and the exhaust gases temperature in the kiln is in the associated lower computational cost when compared to methods such as finite elements or finite differences to obtain the temperature profile. Thus, the feasibility analysis of the coprocessing becomes more simplified, knowing the Arrhenius factors and the activation energy of the reactions of the compounds, and several mixtures of fuels and residues can be simulated in less time, considering the operating conditions.

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