

THERMAL DESTRUCTION EFFICIENCY OF INDUSTRIAL RESIDUES DURING THE COMBUSTION IN THE ACTIVITY OF CO-PROCESSING IN ROTARY KILN OF CEMENT INDUSTRY

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Abstract: *In the last decades, the generation of industrial wastes has increased, creating a great concern about its appropriate storage and destruction. In this context, the activity of co-processing of industrial wastes in rotary kilns of cement plants constitutes an alternative for the thermal destruction of industrial wastes, efficiently, if attended the thermodynamic and chemical requirements for the process. For the clinker production it is necessary that the raw material reaches temperatures around 1450°C. For this, inside the rotary kiln the flame temperature should be close to 2000°C. In the precalciner where happens the secondary burning of fuel, the temperatures are around 900 to 1000°C. The co-processing can consist of the partial substitution of the primary fuel used in the kiln, usually of fossil origin, for an industrial waste with reasonable calorific value. During the burning process it happens, at the same time, the thermal destruction of the waste and the use of the heat liberated in the process. Another form to co-processing is the substitution of part from the raw material by an industrial waste, of low or much reduced calorific value, whose hazardous constituents or non-inert compounds are destroyed, when they reach the high internal temperatures of the kiln. This way, this work discusses the efficiency of destruction of industrial wastes, being based in the related calculations from the chemical equilibrium and the chemical kinetics, of components wastes, considering the combustion temperatures and the residence times of gases, inside the rotary kiln, in the precalciner and in the cyclones preheater. It is still discussed, the change of the types of used primary fuels and its effects in the efficiency of destruction of the co-processed wastes. The results of the calculations from the chemical equilibrium and from the chemical kinetics demonstrate that certain residues cannot be co-processed in the precalciner or in the ascension tower of rotary kiln system, due to the low efficiency of thermal destruction there, creating the possibility of emissions of pollutants for the environment. Also, the results show high destruction efficiency for the residues introduced in the main burner. The place of residue feeding is adapted to its destruction, to minimize the pollutant emissions, and it is of fundamental importance.*

Keywords: *Portland Cement, Thermal Destruction, Co-processing.*

1. INTRODUCTION

The increase of society awareness to the respect of the environmental questions and the energetic crisis due to the petroleum shock in decade of 70's, did with that great part of countries from Europe and the North America search for alternatives for fuel oil use, a derived of petroleum used in great scale to the time, to assist the energetic demands of their industrial processes.

The oil crisis also had consequences in Brazil, because the cement industry at the time, used practically, only fuel oil in its rotary kilns. Thus began the search for alternatives to minimize the effects of high oil prices and its derivatives in the economy, and other fuels or mixtures of them were used.

The cement plants began to use coal in rotary kilns, and to a small scale, industrial wastes burned as a source of additional energy. However, even after adjustment of supply and stability of oil prices, these activities persisted, thus changing the profile of the sector with respect to fuels. Subsequently, the petroleum coke began to be used as fuel in cement production.

The co-processing of industrial wastes in rotary kilns of the cement industry has appeared as a new technology of thermal destruction of certain types of industrial wastes. In co-processing, the heat generated by burning of waste is utilized in productive process. The first tests of burning of wastes as fuel in cement kilns were performed in 1970 in the United States; afterwards, this technique has been applied in Europe and Asia, and more recently in Brazil.

Due to the great volume of generated residues, in the decade of 80 there was an increase in the interest of the society in the management of these materials. Standards have been developed for handling, transport, treatment and storage, of industrial wastes to being utilized in co-processing in rotary kilns.

Conscious about the dangerous potential of these residues, the society, government and environmental organisms are inquiring for to control the discard of these materials. Actually the environmental laws are more demanding. Many generators of hazardous industrial wastes are opting for their thermal destruction. The first known technique is the incineration. This technique demands high cost for his implementation. Besides, the incineration generates atmospheric pollution, that need of additional control. In the incineration, the ashes generated are considered dangerous wastes, and they should be discarded in an appropriate way for not damaging the environmental.

In this case, the co-processing technique is viable to destroy wastes. The introduction of industrial wastes as source of energy for the clinker production allows the destruction of the wastes and their ashes are mixed to the product. It is important verify, in function of the chemical characteristics of the waste that will be co-processed, if there are conditions to achieve high level of thermal destruction, in place of the rotary kiln chosen to fed the waste. The amount fed of wastes in the burner of the rotary kiln must be controlled so as not to raise the levels of emissions of pollutants gases and heavy metals. Thus, it is necessary to analyse the physics and chemical characteristics of each waste and its compatibility to the process. It is vital the consideration about the environmental limitations related to atmospheric emissions, safety and hazards regarding use, storage and transport. Additionally, it should be observed the fact that the ashes of the co-processed wastes will be incorporated into the clinker, and this can not change its quality, nor the final product, the Portland cement (Ottoboni et al., 1998).

Basically the process consists of the substitution of a portion of the traditional fuels, such as coal, petroleum coke, fuel oil or natural gas, by industrial waste under certain patterns, which comprises operational and environmental issues. Consequently, there is an economy of energetic resource and also treatment and final disposition of the hazardous waste.

Wastes that have LHV (low heating value) above a minimum value have been applied as alternative, secondary or complementary fuels. This application has been named as co-processing, due to the combination of two processes (the waste burning and the thermal treatment) in one. This waste treatment process tends to present high destruction efficiency, besides being economically viable, because it allows the utilization of waste as alternative fuel and raw material for the fabrication of the clinker, which is the main constituent of Portland cement. The safety of the process is related to both the efficient control of the temperature of the flame and the heat transfer process, as well as the accurate mixture of the raw material, in order to obtain high values of destruction and transfer efficiency (Silva, 1994).

The advantages of co-processing over the conventional incineration are outstanding due to the operational characteristics of rotary kilns on cement plants. The co-processing in the main burn of rotary kiln presents high flame temperature ($\approx 2000^{\circ}\text{C}$) during normal operation, and a long residence time at high temperature, which guarantees a great efficiency of thermal destruction. Additionally, it should be considered the alkaline characteristics of the raw material (neutralization of the cloridric acid or others compounds), the incorporation of the ash to the clinker (which promotes the immobilization of the heavy metals) and reduction of other costs (Silva et al., 1993). Due to alkaline atmosphere, when the raw materials present low pyrite tenor, it is possible to use fuels with larger content of sulfur in rotary kilns, with low emission of sulfur dioxide. The large amount of lime and calcium oxide allows the retention of sulfur dioxide by the formation of CaSO_4 .

2. THERMAL DESTRUCTION OF INDUSTRIAL HAZARDOUS WASTE

In the co-processing, the wastes with hazardous compounds should be treated with high efficiency. The wastes should stay for an enough time for the destruction to happen.

The rotary kilns of clinker production have favorable conditions for the thermal destructions of wastes, if satisfied the restrictions of the process. The combustion gases stay in the interior in this type of equipment enough time in high temperatures, and the flame temperature is around 2000°C in principal burner, allowing the thermal destruction of possible dangerous compounds to the human health. Up to 60% of the necessary heat it is introduced for the it burns of fuels inside the precalciner (3), as shown in Fig. 1, being the rest introduced in the main burner of the rotary kiln (4). The tertiary air is led by an external duct, in temperature above 700°C , heat recovery of cooler clinker, allowing the maintenance of the temperature in inside the precalciner between 900 and 1000°C . Most of the necessary heat to the process is introduced in the precalciner, allowing the occurrence of limestone calcination, an endothermic reaction.

In another kiln type, with cyclones preheaters, almost all the necessary fuel to the process will be introduced in the burner of the rotary kiln, in high temperatures. For several types of industrial hazardous wastes the destruction in these kilns tends to happen with larger efficiency, due to increase of the residence time in high temperature.

The cement industries are introducing several types of wastes in the precalciner. This activity should be analysed with caution. The temperature in this equipment is not elevated as it happens in the kiln. More resistant compositions cannot have temperature for their destruction. The temperature inside a precalciner varies between 800 and 1000°C .

Like this, some compounds cannot be destroyed in the atmosphere inside of the precalciner, and being emitted, they can cause damages to the human health and the environment.

In this work the thermal destruction feasibility will be investigated in six compounds commonly found in industrial residues (as it will be showed on Tab. 1).

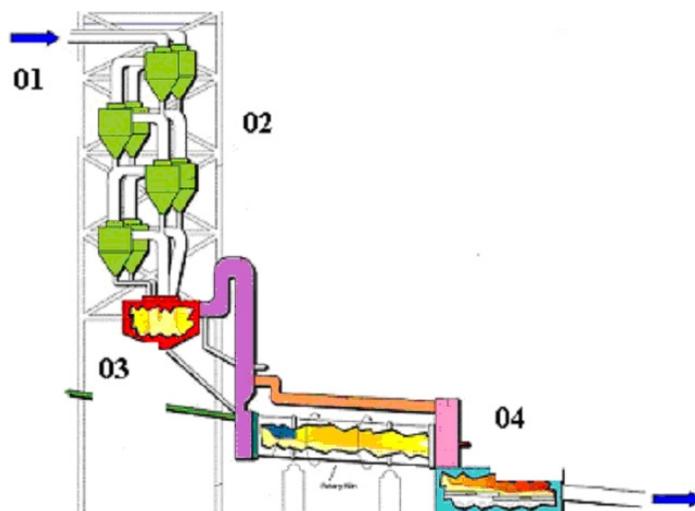


Figure 1 - Portland Cement Process: 01) introduction of raw materials; 02) cyclones preheaters; 03) precalciner with tertiary air; and 04) burner of rotary kiln and cooler clinker.

3- CHEMICAL KINETICS

In thermodynamics, the variation of the Gibbs free energy of supplies provides a criterion to evaluate the spontaneity of a chemical reaction. This study allows affirming the occurrence of a reaction in a given condition of temperature and pressure analyzed.

If a reaction happens, how long time does it takes? The chemical kinetics allows knowing the speed of the reactions and the factors that influence such as, pressure, temperature and concentration. For the kinetics, the speed of the reactions can be divided in three groups: extremely fast reactions, extremely slow reactions and reactions of moderate speeds.

In the last decades, the study of the kinetics allowed the progress of the technology of combustion, allowing the development of complex systems.

The interpretation of the chemical processes is fundamental for the study of the combustion. The reaction rates control the combustion rates, the formation rates and the destruction of pollutants (Turns, 2000).

The speed or the rate of a generic chemical reaction, can be obtained by Eq. (1) (Signoretti, 2008).

$$v = -\frac{1}{\nu_A} \frac{dC_A}{dt} = -\frac{1}{\nu_B} \frac{dC_B}{dt} = +\frac{1}{\nu_C} \frac{dC_C}{dt} + \frac{1}{\nu_D} \frac{dC_D}{dt} \quad (1)$$

Eq. (1) can be put in a more general way:

$$v = \mp \frac{1}{\nu_i} \frac{dC_i}{dt} \quad (2)$$

where v is the speed or the reaction rate, the signs (+ and -) refers to the reagents and products respectively, and it is the stoichiometric coefficient, and C is the concentration of the component i of the reaction.

The equalities of Eq. (1) indicate that any concentration relationship with the time can be taken as a definition for the reaction speed, independent of treating with reagents or products.

The reaction speed Eq. (2) can be obtained through the law of the action of the masses: the speed of a chemical reaction is equal to the product of a constant, called the rate constant, by the active masses of the reactants, elevated to their stoichiometric coefficients. This statement is equivalent to the Eq. (3):

$$v = k C_A^{v_A} C_B^{v_B} \dots \quad (3)$$

Comparing the two definitions one has:

$$v = \mp \frac{1}{\nu_i} \frac{dC_i}{dt} = k C_A^{v_A} C_B^{v_B} \dots \quad (4)$$

Eq. (3) and (4) has its validity restricted, actually, to the cases of the elementary reactions, as the reactions that happen in a single step, presenting the reaction order of each species identical to the stoichiometric coefficient of each species for reaction (Pereira Neto, 2004 apud Signoretti, 2008).

The complex reactions are formed by a group of elementary reactions, each one of them happening in a single step (Levenspiel, 2000). However, to adjust the experimental data to the calculated values, does the kinetic law uses exponent α and β , what are in general different from the stoichiometric coefficient of the chemical equation. Eq. (3) is transformed into Eq. (5).

$$v = k C_A^\alpha C_B^\beta \dots \quad (5)$$

The coefficients α and β can be whole or fractional numbers, positive, negative or even null. The constant of speed (k), in the Eq. (5) is an exponential function of the temperature and it can be written in agreement with Eq. (6) known as Arrhenius Equation.

$$k(T) = A e^{\left(-\frac{E_a}{RT}\right)} \quad (6)$$

Where A is the pre-exponential factor or frequency factor, E_a is the energy of activation of the reaction, R is the universal gas constant and T is the temperature of the system. Other expressions similar to the Arrhenius Equation Eq. (6) are found in the literature as Eq. (7) derived from the theory of the transition state (Fogler, 2002, and Hill and Smoot, 2000):

$$k(T) = AT^n e^{\left(-\frac{E_a}{RT}\right)} \quad (7)$$

In Eq. (7) the value of the exponent n is among 0 and 1. Usually the constant of speed is given in function of the following units, according to Eq. (8):

$$[k] = L^{n-1} \cdot \text{mol}^{n-1} \cdot \text{s}^{-1} \quad (8)$$

Where n is the sum of the exponents, as showed in Eq. (9).

$$n = \alpha + \beta \quad (9)$$

3.1 – First order reactions.

Considering a generic reaction:



Applying the definition of speed or reaction rate in Eq. (10) one obtains:

$$\frac{dC_A}{dt} = -k C_A^\alpha \quad (11)$$

For first order reactions $\alpha = 1$, and in Eq. (11) separating the variables and integrating one obtains:

$$\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = -k \int_0^t dt \quad (12)$$

$$\ln \left(\frac{C_A}{C_{Ao}} \right) = -kt \quad (13)$$

Applying the exponential on both sides of Eq. (13), it results in Eq.(14).

$$\left(\frac{C_A}{C_{Ao}} \right) = e^{(-kt)} \quad \text{ou} \quad C_A = C_{Ao} e^{(-kt)} \quad (14)$$

where C_A is the final concentration of the specie A and C_{Ao} its initial concentration.

The calculation of the time for a reaction of first order can be obtained substituting the Eq. (7) in Eq. (13), being obtained Eq. (15).

$$\ln \left(\frac{C_A}{C_{Ao}} \right) = -A e^{\left(-\frac{E_a}{RT} \right) t} \quad (15)$$

Rearranging the last expression is obtained:

$$-\frac{1}{A} \left[\ln \left(\frac{C_A}{C_{Ao}} \right) \right] = e^{\left(-\frac{E_a}{RT} \right) t} \quad (16)$$

Applying the logarithm on both sides of the Eq. (16) one obtains:

$$\ln \left\{ -\frac{1}{A} \left[\ln \left(\frac{C_A}{C_{Ao}} \right) \right] \right\} = -\frac{E_a}{RT} + \ln t \quad (17)$$

Applying the exponential on both sides of the Eq. (17) and rearranging the expression it is obtained the Eq.(18), that allows to calculate the time to reaches a given concentration for a compound in a first order reaction. For a given compound it is possible to calculate the time request to reach a given level of destruction for that compound, if the E_a , A and $C_{A,0}$ parameters, are known.

$$t = \exp \left[\ln \left\{ -\frac{1}{A} \left[\ln \left(\frac{C_A}{C_{Ao}} \right) \right] \right\} + \frac{E_a}{RT} \right] \quad (18)$$

4- MATERIALS AND METHODS

In the preliminary evaluation of the residues that can be co-processed in a cement kiln, it should be sought in composition those substances with larger difficulty for their destruction. With these data, and knowing the kinetic parameters of the reactions involved in their destruction, it can be calculated for each temperature the necessary time for a high efficiency of destruction of their compositions. Some dangerous compounds have been considered in this work, in order to show the risks of a wrong choice of the location for its burning. To know the destruction efficiency in the kiln of Portland cement production, the parameters shown in Tab. 1 were used. These parameters were introduced in the equation of residence time to obtain destruction efficiency around of 99.99% for each temperature of the gaseous phase.

The residence time in a certain temperature permits to evaluate if an organic compounds would be indicated to be introduced in the precalciner. The results of these calculations are showed in the Fig. 2 to Fig. 7.

Table 1 - Characteristics of the hazardous organic compounds used as secondary fuels in rotary kiln of clinker production.

Organic Compounds	Chemical Formula	Kinetics Parameters ⁽¹⁾		Use and Applications ⁽²⁾
		Pre-exponential Factor A (1/s)	Activation Energy Ea (J/kmol)	
Toluene	C ₇ H ₈	2.1 x 10 ¹²	324.5 x 10 ⁶	Raw material starting from which one obtains derived of the benzene, coloring, perfume, TNT and detergents. It is added to the fuels (as antiknock) and as solvent for paintings.
Xylene	C ₈ H ₁₀	4.2 x 10 ¹²	324.4 x 10 ⁶	Solvents and precursors of other chemical products
Cresol	C ₇ H ₈ O	1.0 x 10 ¹⁰	293.0 x 10 ⁶	Disinfecting, pigment and insecticides.
Chlorobenzene	C ₆ H ₅ Cl	1.9 x 10 ¹⁶	303.9 x 10 ⁶	Herbicides Production, pigment and rubber.
Hexaclorobutadiene	C ₄ Cl ₆	2.1 x 10 ¹²	324.4 x 10 ⁶	Solvents, Algicide and Herbicide
Maleic Anhydride	C ₄ H ₂ O ₃	1.0 x 10 ¹³	293.0 x 10 ⁶	Production of additive for lubricating oils; insecticides, herbicides and fungicides.

Fonte: ⁽¹⁾ Castaldini (1986) ⁽²⁾ Passow (2003).

5- RESULTS AND DISCUSSIONS

The investigated organic compositions and presented in the Tab. 1, can be present in the composition of the industrial residues to be co-processed in rotary kilns for the production of Portland cement as secondary fuels.

The introduction of these residues should happen in the rotary kiln and not in the precalciner. In agreement with these results, the introduction of these residues in the main burner of the rotary kiln will allow to reduce the risks of the process, due to high efficiency of destruction. Due to the necessary time is very inferior to the available in that point of the rotary kiln, the destruction will be above 99.99%. The results presented in the Figures 2 to 7 show that the organic compounds stay for enough time so that it reaches the intended destruction level (99.99%).

The organic compounds as chlorobenzene and maleic anhydride need a very small residence time and therefore they are destroyed quickly in the clinker kiln. Therefore, the time of residence of the compounds chlorobenzene (Fig. 7) and maleic anhydride (Fig. 6) in the temperature of 2273K is of 7.0 x 10⁻⁹ seconds and 7.5 x 10⁻⁶ seconds, respectively.

However, organic compounds as hexaclorobutadiene (Fig. 3) and toluene (Fig. 4) need a residence time larger when compared to the organic compounds chlorobenzene and maleic anhydride. The residence time of the compounds hexaclorobenzene and toluene in the temperature of 2273K is around 1.9 x 10⁻⁴ seconds. In the temperature of 2273K, the cresol needs a time of 7.5 x 10⁻³ seconds to obtain a destruction efficiency of 99.99% (see Fig. 7).

In the temperature of 1173K (temperature in the precalciner), only the chlorobenzene compound (Fig. 7) presents favorable conditions to its introduction in the precalciner.

Therefore, the residues that contains the compounds: xylene, toluene, hexaclorobenzene, cresol and maleic anhydride, accord with results shown in Fig. (2) to Fig. (6), are not able to be introduced in the precalciner of the cement kiln.

Among the compositions, the worst case is that involving the cresol compound. This compound needs 15430 seconds to be destroyed at a level of 99.99% of efficiency, as presented in the Fig. 5.

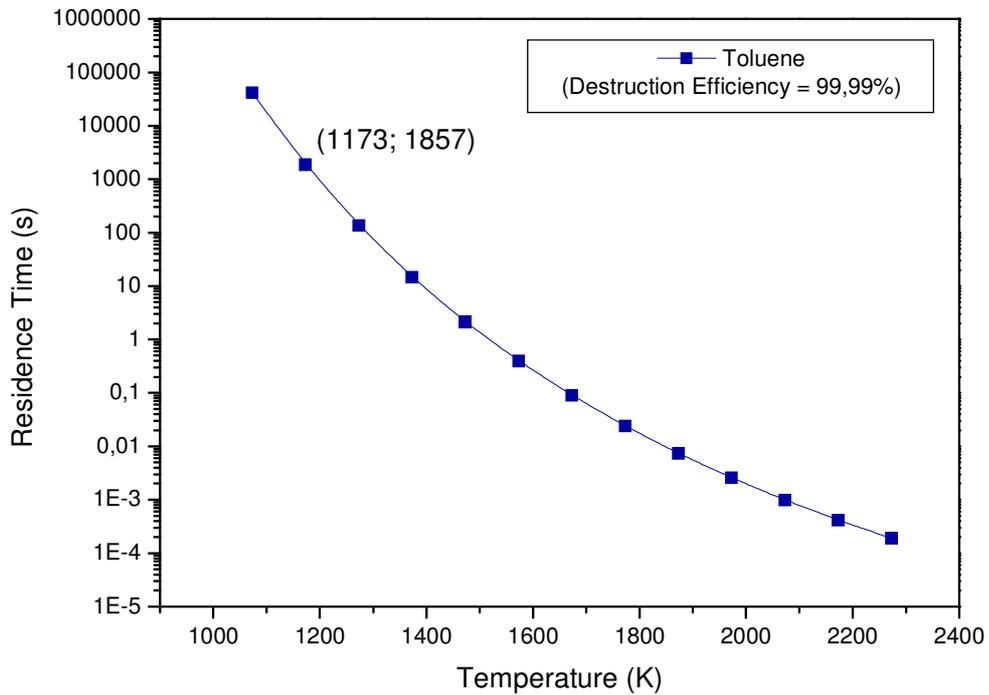


Figure 2 – Variation of temperature and residence time for destruction efficiency of 99.99% for toluene in a rotary kiln of clinker production.

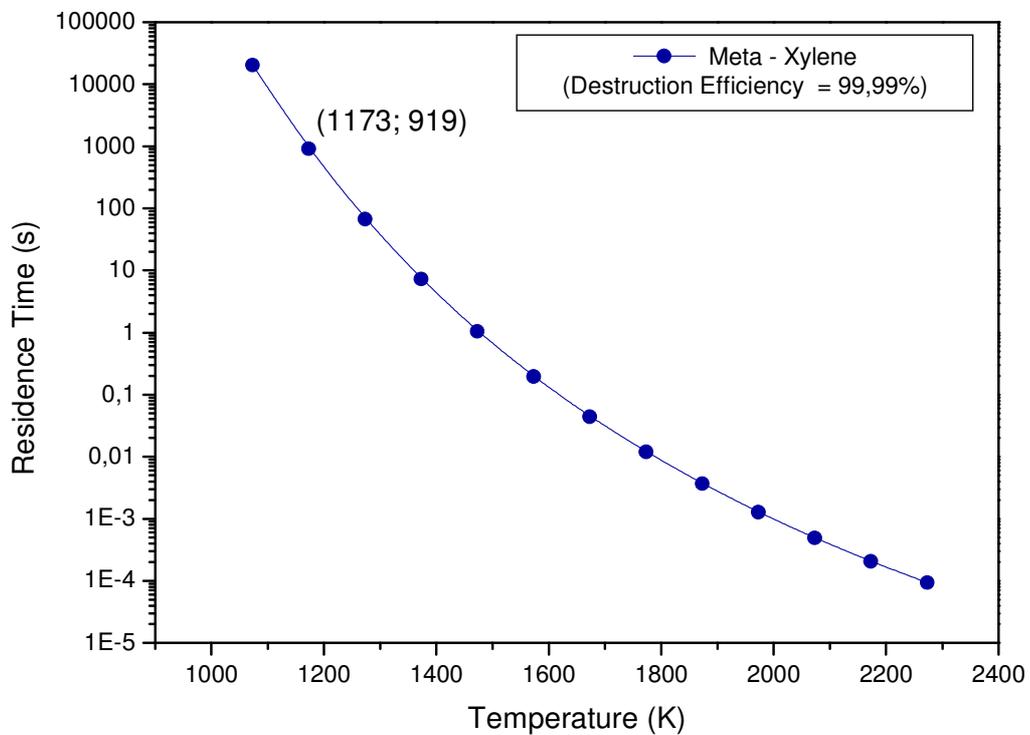


Figure 3 – Variation of temperature and residence time for destruction efficiency of 99.99% for meta-xylene in a rotary kiln of clinker production.

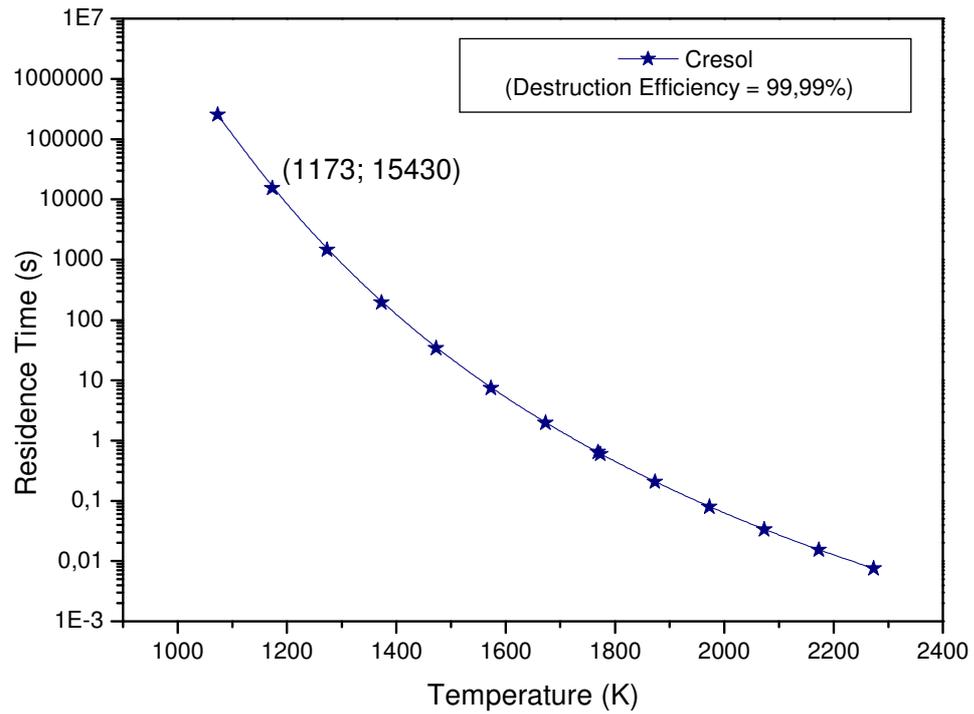


Figure 4 – Variation of temperature and residence time for destruction efficiency of 99,99% for cresol in a rotary kiln of clinker production.

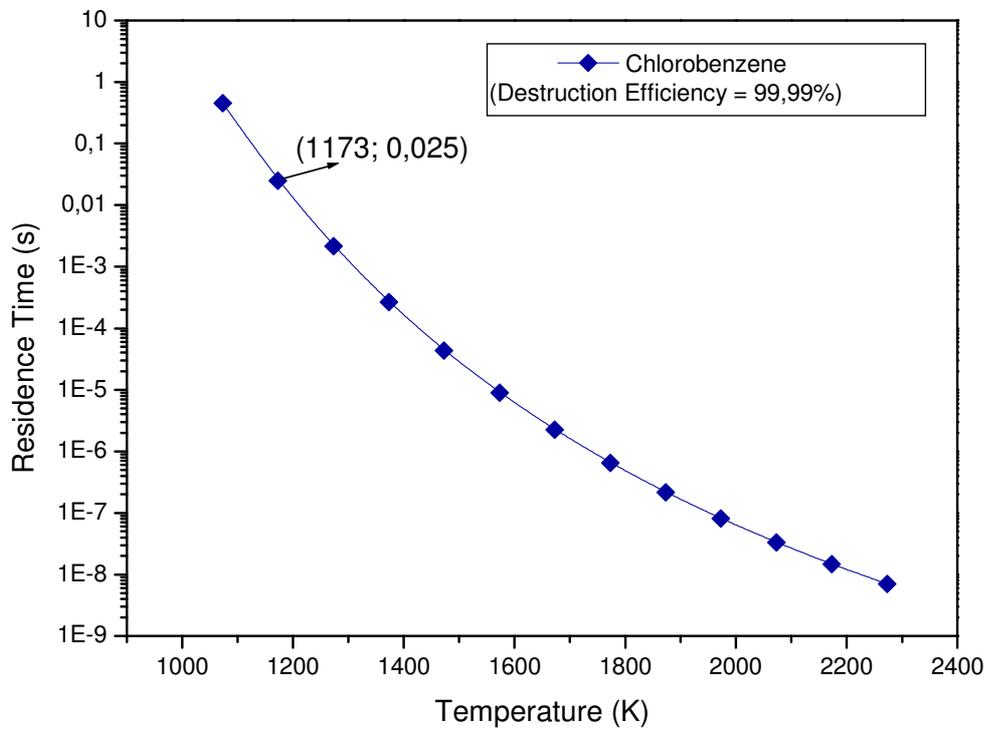


Figure 5 – Variation of temperature and residence time for destruction efficiency of 99,99% for chlorobenzene in a rotary kiln of clinker production.

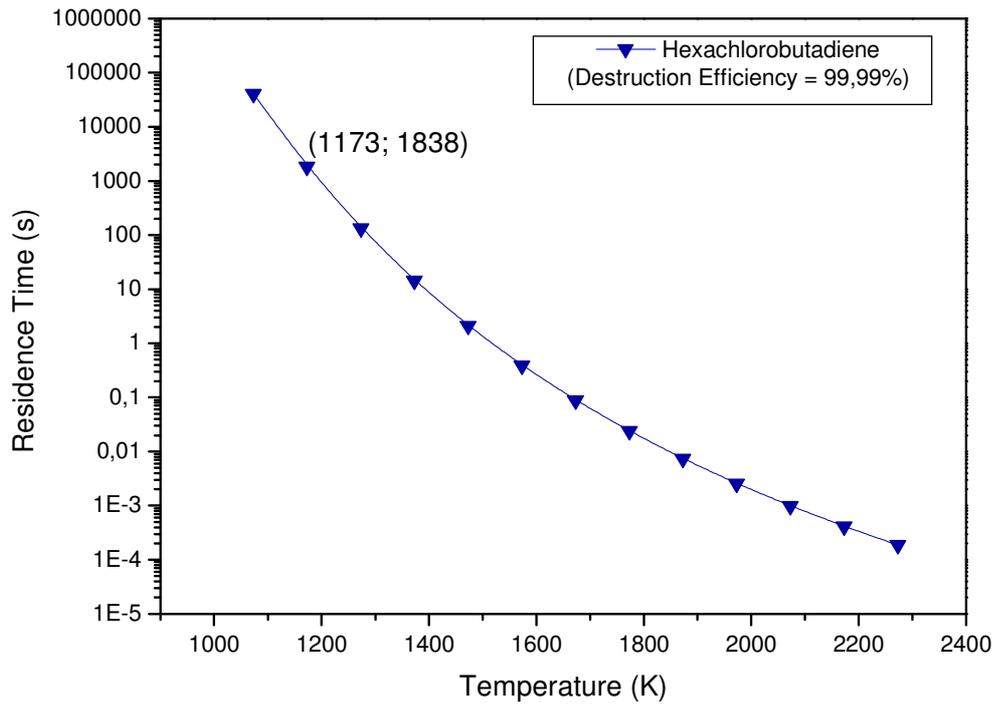


Figura 6 – Variation of temperature and residence time for destruction efficiency of 99.99% for hexachlorobutadiene in a rotary kiln of clinker production.

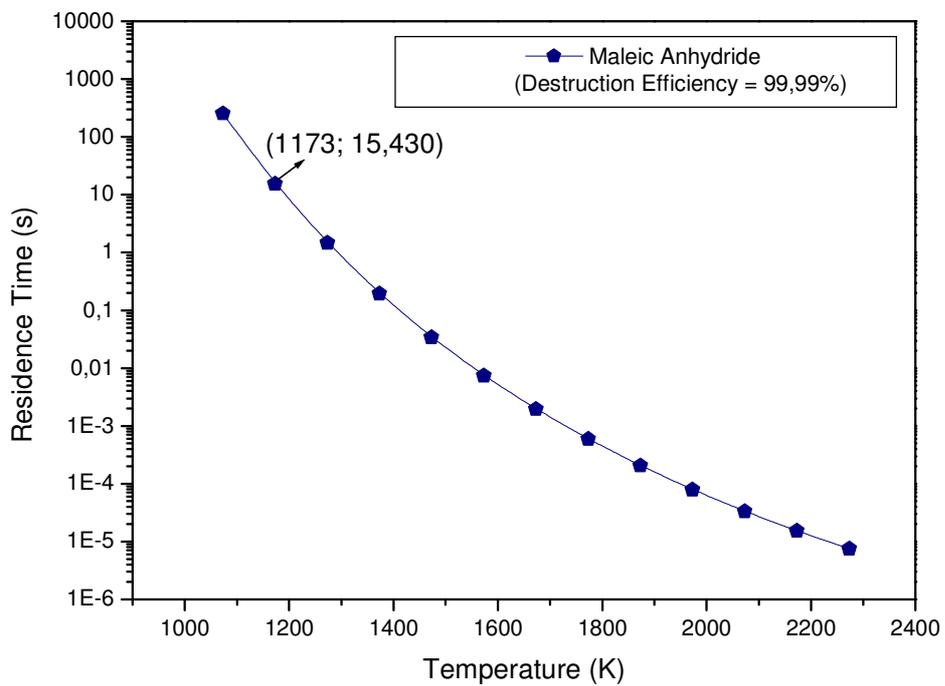


Figura 7 – Variation of temperature and residence time for destruction efficiency of 99.99% for maleic anhydride in a rotary kiln of clinker production.

6- CONCLUSIONS

From the organic compounds studied in this work, the xylene and toluene found in industrial wastes as contaminants, can be destroyed inside the rotary kilns used in the clinker production. However, it must be chosen the place for the feeding of these compounds to be the precalciner for technical reasons, the thermochemical behavior of the compounds of the residues should be analyzed in the operational conditions, in low temperatures and small times of residence, and with the presence of catalysts.

The introduction of these materials (residues) outside the main burner of the rotary kiln, where the temperatures reach values between 1800 and 2000°C, can damage the safety of the process.

As the time of residence of the compositions in the precalciner is not elevated and the temperatures in its inner vary between 800 and 1100°C, it is not advisable burning of several types of residues in the precalciner. This way, whenever if it intends to begin the co-processing, or to make an evaluation of the process or even to alter the burning of residues, it should be analyzed if there are dangerous components that demand high temperatures for their destruction.

Based in safety operational conditions, from the substances studied in this work, only the organic compound chlorobenzene can be introduced, with safety, in the precalciner.

Hence, the environmental licensing of co-processing of residues with the compounds studied in this work should be liberated only to burn in the Portland cement rotary kiln. In the temperatures reached in this kiln (2273 K), the necessary time for the efficient destruction is small, as presented in this work.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

- Castaldini, C. et al., 1986, Disposal of Hazardous Wastes in Industrial Bolilers and Furnaces, New Jersey U.S.A., Noyes Publications, 429p.
- Fogler, S. C. 2002. “Elementos de Engenharia das Reações Químicas”. LTC (Grupo GEN).
- Hill, S. C. and Smoot, L. Douglas. 2000. “Modeling of nitrogen oxides formation and destruction in combustion systems”. Progress in Energy and Combustion Science 26, 417–458.
- Levenspiel, O., 2000, Engenharia das Reações Químicas, Edgard Blucher, 3 ed. 563p.
- Ottoboni, A.P., Souza, I., Menon, G.J., Silva, R.J., 1998, “Efficiency of Destruction of Waste Used in the Co-incineration in the Rotary Kilns”, Energy Conver. Mgmt., Pergamon, Elsevier Science Ltd., Vol. 39, No. 16-18, pp. 1899-1909.
- Passow, N. R., 2003, “Regulatory Agencies, Chemical Process Industry”, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons Inc.
- Signoretti, V.T., 2008, “Control of NO_x, SO_x and Heavy Metals Emissions When Alternative Fuels Are Used And of High Sulfur Content in the Cement Industry”. Itajubá, 265p. DSc Thesis - Instituto de Engenharia Mecânica, Universidade Federal de Itajubá, Brazil, (In portuguese).
- Silva, R.J., 1994, “Energetic Analysis of Production Plants of Portland Cement”, PhD Thesis, Estadual University of Campinas, Faculty of Mechanical Engineering, Campinas-SP, Brazil, (In portuguese).
- Silva, R. J., Nebra, S. A. and Rossi, L. F. S., 1993, “Emission and Control of Pollutants in Cement Industry”, Third International Conference on Waste Management in the Chemical and Petrochemical Industries; Salvador, BA, Brazil, CETREL S.A., IAWQ, Vol. I, pp. 363-370.
- Turns, S. R. (2000), *An Introduction to Combustion: Concepts and Applications*, McGraw-Hill Book Co - Singapore, 2^o ed., 676p.

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