

Dioxin and Furan Formation and Destruction in Rotary Kiln Used In Waste Co-Processing

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ABSTRACT

More and more, the cement industries have used their rotative kilns for the destruction of industrial residues. In the time that the demand of residues for the co-processing grows in these kilns, also increases the concern which refers to the pollutants emissions. It is known that to burn wastes which contain materials with presence of halogens above of certain levels can contribute to the production of organic composites known as dioxins and furans. The cement kilns are really a good option for co-processing because the residence time of the gases in its interior is big enough to guarantee a complete destruction of organic composites, but depending on the type and where the residues are introduced, it cannot have a great condition for the dioxins and furans destruction. This article look for to do an analysis of the factors that get the dioxins and furans formation inside the rotative kilns, considering the restrictions with relationship to the types of co-processed residues, the percentage of substitution of traditional fuels, feeding points, and control equipments. The analysis of temperature profiles and of the time of permanence of the gases in the different internal zones of the kiln allows an accompaniment of the reactions involved in the process of it burns.

Key words: Dioxins, Furans, Cement, Kinetics, Combustion.

INTRODUCTION

Dioxins and furans are cyclic chemical organic composite that can cause damages to the animal health due to its toxicity. They are formed by burning of fuels or co-processed residues that contain chlorides, cyclic organic chains, and organo-chlorinated, and they are emitted together with the gases and emanated particles of the process. Due to its toxicity, they are classified as dangerous pollutants, whose the formation should be avoided or minimized, so that its concentration in the environment is in tolerable levels for the health of animals and people.

When we speak in dioxins and furans we will be referring to the chlorinated composites, which are healthy very toxicant and exist more than 200 different variants of them. However, when in the burning process with necessary and enough conditions for the formation of them, several types are formed simultaneously. Therefore, if there is the formation of dioxins and furans not toxicant or not very toxicant, there will also be the formation of toxicant compositions among them.

The Figures. 1 and 2 show the 2,3,7,8 tetrachlorinedibenzodioxin (TCDD) and tetra

chlorinated dibenzofuran (TCDF), respectively, the more toxic organo-chlorinated composites of the family of the dioxins and furans. Chlorine or other atoms, halogens or not, can take any positions of the and furan dioxins molecules, forming more than 200 configurations as it was already said. Dioxins and furans are not soluble in water and they are solid in normal temperature; they are usually attached to the soil or on particulates material disposed near the formation places.

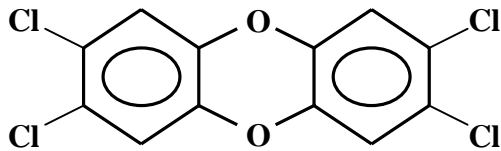


Figure 1 –TCDD Representation

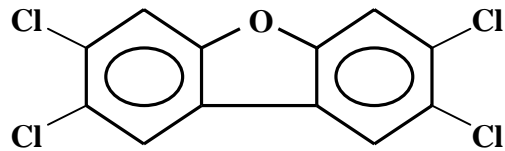


Figure 2 – TCDF Representation

TOXICITY

To illustrate how these composites are toxicant, a total dose of 6mg of the 2,3,7,8, TCDD is already lethal for a mouse (Paddock, 1989). The toxicity of the dioxins and furans vary a lot among the species and the degree of toxicity of them is not known for the human species with a lot of certainty. In people exposed at elevated levels of 2,3,7,8, TCDD effects verified varied in the health, which most disappeared after the exposition, except a stain type in the skin that persisted per decades. A short exposition to a high concentration of dioxins and furans (present in fumes originating from burns of chlorinated organic materials, for example) can be harmful, but very worse is the prolonged exposition to a smaller concentration, insufficient to cause immediate damages, but that will accumulate in the organism with elapsing of the time. Dioxins and furans can cause cancer, formation defects, abortions, effects in the reproductive system and of defense, and to get to the death. Another complicated factor is that dioxins and furans are not destroyed by the human body and they are bio-accumulative, therefore, exposition to the low dose certainly will cause serious consequences in elapsing of years.

For have a mensuration of the toxicity of the several dioxins and furan types, the concept of Toxicity Equivalent (TEQ) was created. For it, the toxicity of the several dioxins and furan types are compared with the TEQ of 2,3,7,8 TCDD which is known by being the more toxic of every dioxin and furan. In this way a table of Equivalent Toxicity can be set up with which will be possible to calculate the toxicity of a dioxins and furan mixture emitted by any process that is being object of studies. The following Table 1 shows the chlorinated dioxins and furan TEQs extracted from the report of EPA (EPA-454/R97-003).

In general, the determination of the risk to the human health caused by the toxicity of a dioxins and furan mixture involves the following steps:

1. qualitative and quantitative chemical analysis of dioxins and furans in a sample;
2. multiplication of the concentration of each congener in the sample for TEQ to express the concentration in terms of equivalent of 2,3,7,8-TCDD for each one of them;
3. To add all the results of the previous stage to obtain the total of equivalent of 2,3,7,8-TCDD;
4. determination of the human exposition to the mixture in study, expressed in terms of equivalent of 2,3,7,8-TCDD;
5. combination of the human exposition with the information on toxicity of the 2,3,7,8-TCDD to esteem the risks associated with the mixture.

TABLE 1 – International Toxicity Equivalent Factor (I-TEQs)

Configuration	I-TEQs
Dioxins	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.001
Furans	
2,3,7,8-TCDF	0.1
2,3,4,7,8-PeCDF	0.5
1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.001

T=tetra; Pe=penta; Hx=hexa; Hp=hepta; O=octa; C=Cloro; D=Dioxin; F=Furan

It is important to say that the qualitative and quantitative chemical analysis of dioxins and furans in a sample are a delayed process, very expensive and that few laboratories in the world have conditions to accomplish this task, because it demands last generation instruments and very specialized personal. Typically, since the beginning of the collection of samples to the final result is taken on the average 3 months of work (Brian Gullett and Randy Seeker, 1997).

The Program of the Nations United to the Environment recommends that the tolerable maximum of dioxins and furans in a pollutant source are of 1 ng TEQ/Nm³ (Ueno et ali., 1997).

HOW ARE FORMED DIOXINS FURANS ?

Chlorinated dioxins and furan are not formed intentionally. Their formation reactions happen in atmospheres where exist necessary and enough conditions that allow a complicated pathways of combinations which finish with the dioxins and furan formation that are composed quite stable, more than its precursors. The processes where the combustion of chlorinated materials happens or where exist the chlorinated intermediates formation possess conditions that can take to the dioxins and furan formation in some part of the process. The formation of chlorophenol and their reaction with chlorobenzene take to the dioxins formation. Polivinil Chloride (PVC) when burned produces a small amount of chlorobenzene in the pyrolysis, which burns in the presence of air forming dioxins and furan. Policlorinated phenols form dioxins when burned in high temperatures and policlorinated biphenils (PCB) produce furan when burn in presence of air. The pyrolysis or combustion of chlorinated phenols in atmospheres poor of oxygen stimulate the dioxins formation indicating that its formation is part of the mechanism of the complete thermal decomposition of policlorinated phenols in water, CO₂, etc., and of the formation of precursors of the dioxins (EPA-454/R97-003). It is possible to illustrate this formation mechanics as described in the following Fig. 3.

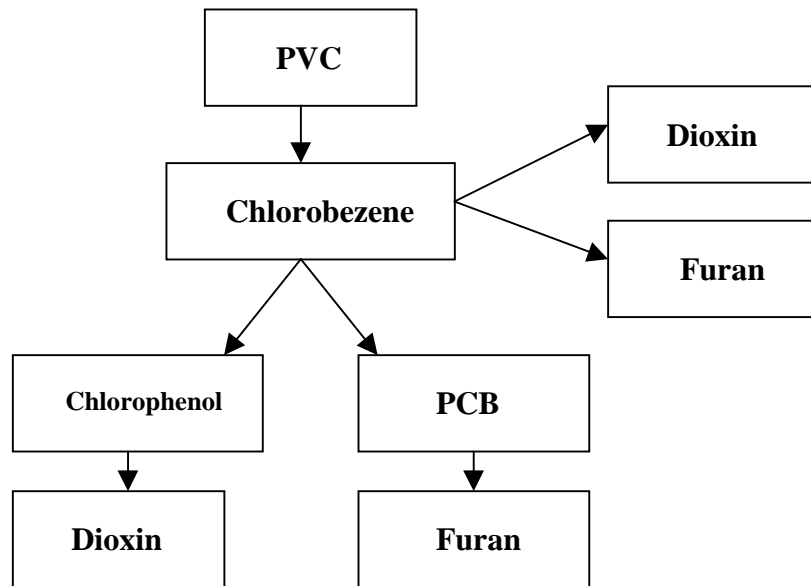


Figure 3 – Dioxins And Furans Formation From Precursors

Here are enumerated three factors that take to the dioxins and furan formation in combustion systems, to know:

1. The incomplete destruction of dioxins and furan present in the fuel – if the combustion is inefficient, a dioxins and furan portion can escape from the system, however a good relation of air/combustible and the temperature are enough to destroy most of the dioxins and furan present in the fuel; the levels of dioxins and furan emissions by incomplete burn are smaller when compared to the other two following factors;
2. Formation inside kilns of the dioxins and furans starting from precursors – it is when there are the dioxins and furan formation during the combustion process; in a burn reaction, several hydrocarbon rings are formed in the intermediary stages of the combustion and they are called precursors; if there is chlorine in the atmosphere, there is the possible reaction of it with these precursors, forming dioxins and furans; the most frequent precursors are chlorobenzenes, chlorophenols and polichlorinated biphenils (PCB); many studies have shown a correlation between the presence of chlorine and dioxins and furan emissions during combustion tests (EPA-454/R97-003), but it is important to remind that the presence of chlorine is a necessary condition for the furans and dioxins formation, but it is not an enough condition; however, when the conditions of burning are good, there is little or any dioxins and furan formation; studies have shown a strong correlation between the emissions of carbon monoxide and the dioxins and furan emissions, what indicates that when the burn conditions are bad there will be good conditions for the dioxins and furan formation;
3. The dioxins and furan formation in low temperatures in the combustion gases that pass inside of the pipes or through the equipments of pollution control – it is when does not have a good burn of the fuel or combustible waste, and there are hydrocarbon formation; then there are the posterior formation of dioxins and furans in another parts of the industrial process, where the temperatures are smaller and elements that can catalyse the formation reactions exist; there are evidences that aromatic rings combine with carbon and

inorganic chlorine present in the fly ashes synthesizing dioxins and furan; these reactions happen between 200 and 500 °C being more expressive in close temperatures of 300 °C; superior temperatures to 500 °C are already enough to begin the fast decomposition of the dioxins and furan.

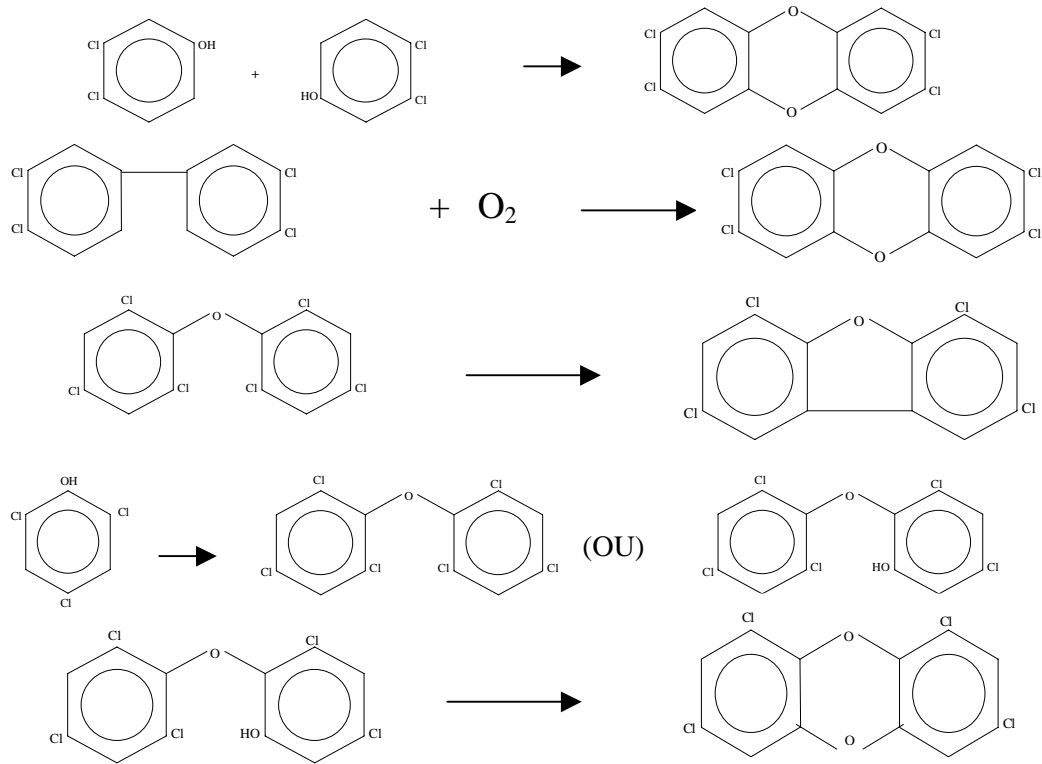


Figure 4 – Some Dioxins and Furans Formation Mechanisms

KINETICS OF DESTRUCTION OF DIOXINS AND FURANS

There are evidences that the dioxins and furan molecule do not resist approximately under superior temperatures the 500 °C. Perhaps an ambient with atmosphere where there are smaller temperatures is unsuited for their permanence. Collina et. ali., (1995), made a study with octachlorinedibenzofuran and octachlorinedibenzodioxin, OCDF/OCDD, in atmospheres whose temperature varied from 200 to 350 °C. For this study they suggested that the molecules mechanism of destruction of OCDF/OCDD follows two ways: the molecule deschlorination for molecules with less chlorine, following intermediary stages, and the molecule decomposition.

For the deschlorination the detected stages were, for dioxins and furans, respectively:



Table 2 – Relation C_R/C_R^0 to the OCDF in diferents temperatures

Temperature→ Time(min.)↓	200 °C	228 °C	250 °C	300 °C
0	1.0	1.0	1.0	1.0
15		0.108	0.067	0.0119
30	0.518	0.066	0.039	0.0041
60	0.340	0.063	0.033	
90	0.173			

The amounts of dioxins and furans with less than 4 atoms of chlorine was very small to be detected in the study. The variation of the concentration of OCDD and OCDF only depend on the concentration of this reagent, being a first order reaction, whose equation that describes the decomposition can be given for:

$$\frac{C_{Cl}}{C_R^0} = \alpha[1 - \exp(-k_{Cl} \cdot t)] \quad (1)$$

where: C_{Cl} is the concentration of the deschlorination products, C_R^0 are the initial concentration, k_{Cl} the equilibrium constant of the deschlorination reaction and t the time.

Table 3 – C_R/C_R^0 Relation to OCDF and Intermediates Composites at 200 °C

Composite→ Time (min)↓	OCDF	HpCDF	HxCDF	PeCDF	TCDF
0	1.0	0.0051	0.0	0.0	0.0
30	0.518	0.0543	0.0023	0.00016	0.00010
60	0.340	0.1160	0.0112	0.00204	0.00078
90	0.173	0.0527	0.0055	0.00039	0.00006

The sum of the concentrations of the deschlorination products is not the same to the initial concentration, so the other way is the decomposition of the dioxins and furan molecules. This reaction is also of first order:

$$\frac{C_D}{C_R^0} = \beta[1 - \exp(-k_D \cdot t)] \quad (2)$$

where: C_D is the concentration of the products of the decomposition and k_D the equilibrium constant of the decomposition reaction.

Then, if there are two ways for the transformation of the OCDD and OCDF molecules, it can be written as being:



where R' and R'' are the reagents fractions that follow the ways of the deschlorination and of the decomposition, respectively, and $R = R' + R''$ in any time t ; P_{Cl} is deschlorination product and P_D decomposition product.

For reactions of first order, the α and β parameters are, respectively, $C_{R'}^0 / C_R^0$ e $C_{R''}^0 / C_R^0$. Thus, we can write a global equation that describes the destruction of OCDD and OCDF:

$$\frac{C_R}{C_R^0} = \frac{C_{R'}^0}{C_R^0} \cdot \exp(-k_{Cl} \cdot t) + \frac{C_{R''}^0}{C_R^0} \cdot \exp(-k_D \cdot t) \quad (5)$$

The equilibrium constants k_{Cl} and k_D can be obtained from Arrhenius's Equation:

$$k = A \cdot e^{-\frac{E_A}{R \cdot T}} \quad (6)$$

or

$$\ln k = \ln A - \frac{E_A}{RT} \quad (7)$$

where A is the Arrhenius's factor, E_A is the activation energy, R it is the gas's universal constant and T the temperature. According to Collina et ali., (1995), were found the following values for the $\ln A$ and ΔE to the OCDF:

Table 4 – $\ln A$ e ΔE Values

	$\ln A$	ΔE Kj/mol
Decomposition	7.419 ± 3.796	39.50 ± 16.23
Chloration	8.889 ± 5.160	54.52 ± 22.05

Table 5 – C_R'/C_R^0 , C_R''/C_R^0 , k_D and k_{Cl} Calculated Values to the OCDF

Temperature .°C	C_R'/C_R^0	C_R''/C_R^0	k_D	k_{Cl}
200	0,4311	0,5689	0,0471	0,0099
228	0,0716	0,9284	0,2059	0,0067
250	0,0732	0,9268	0,2377	0,0421
300	0,0210	0,9790	0,3162	0,0788

The Fig 5 shows the profile of the OCDF destruction in agreement with the extracted punctual data from the work of Collina et ali., (1995), and constant in the Tables 2 and 3 with the obtained curve from the Eq. 5. The Fig. 6 shows the data adjustment of the experimental values from the Table 3 also created with the data from Collina et. ali.,(1995), where we highlighted the concentration variations of the intermediary compositions. For better visualisation, it was extracted the relative data to the OCDF and it was obtained the Fig. 7.

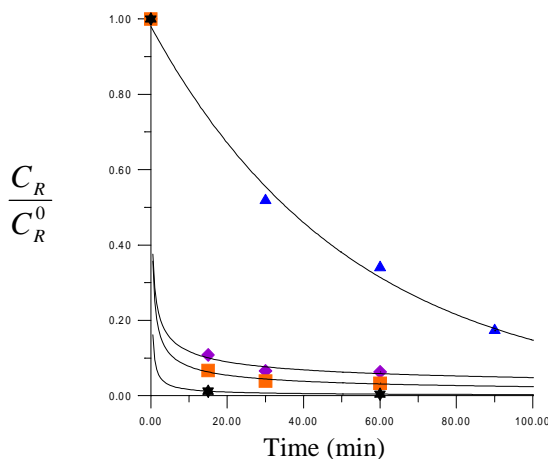


Figure 5 –Destruction Profile of OCDF according to Eq. 5 and Experimentals Datas (Δ - 200°C; \blacklozenge - 228°C; \blacksquare - 250°C; \bullet - 300°C)

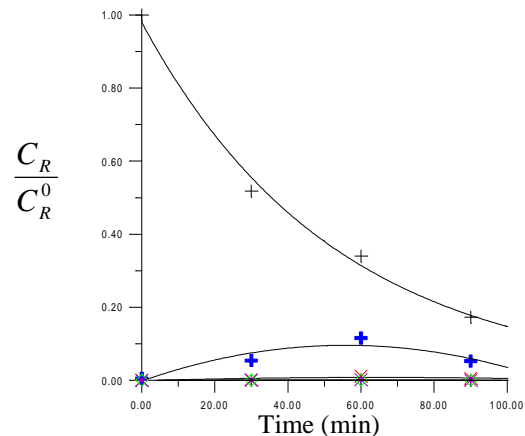


Figure 6 – Destruction Profile of OCDF and Formation and Destruction of Intermediates Composites (+- OCDF; +- HpCDF; x - HxCDF; \diamond - PeCDF; * - TCDF)

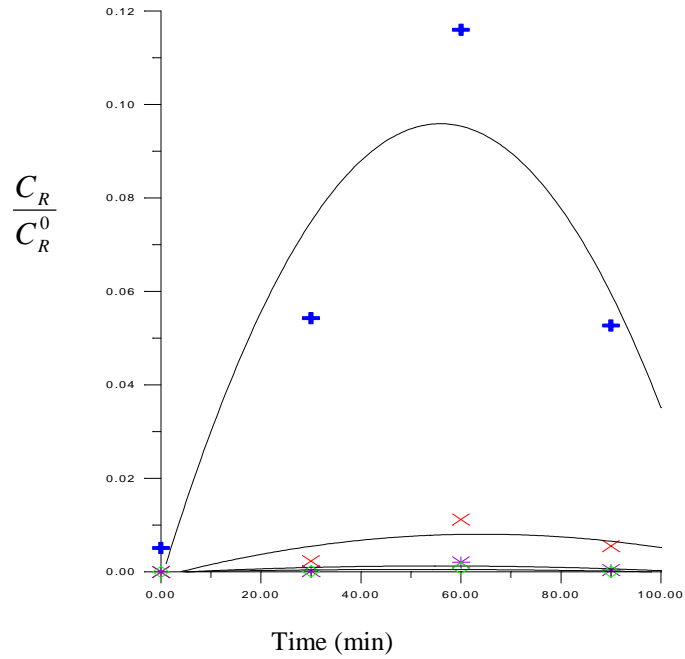
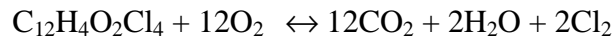


Figure 7 – Destruction Profile of OCDF and Formation and Destruction of Intermediates Composites at 200°C (+- HpCDF; x - HxCDF; ◇ - PeCDF; * - TCDF)

It is possible to see that the decomposition has a preponderant hole in comparison with the dechlorination and this decomposition is greater if the temperature increase.

FORMATION AND DESTRUCTION OF DIOXINS AND FURANS IN CEMENT KILNS

As the decomposition is very bigger than the dechlorination, in order to have a analysis about the dioxin and furan formation in a cement kiln system, it will be very interesting to find out the needed time to the complete decomposition of molecules, that is, to calculate the minimal residence time in the part of system in which the molecule is formed. For the burning of TCDD the following reaction is shown:



The reaction progress is given by the Eq. 8 (Levenspiel, 1991).

$$\frac{\left(\frac{12\varepsilon}{13+3\varepsilon}\right)^{12} \cdot \left(\frac{2\varepsilon}{13+3\varepsilon}\right)^4}{\left(\frac{1-\varepsilon}{13+3\varepsilon}\right) \cdot \left(\frac{12-12\varepsilon}{13+3\varepsilon}\right)^{12}} = \text{Exp}\left(\frac{-\Delta G}{R \cdot T}\right) \quad (8)$$

The Gibbs's Free Energy ΔG is given following:

$$\Delta G(T) = \Delta H(T) - T\Delta S \quad (9)$$

where

$$\Delta H = H_f^o + \int_{T_o}^T C_p(T) dT \quad \text{and} \quad \Delta S = S_f^o + \int_{T_o}^T \frac{C_p(T)}{T} dT \quad (10)$$

The C_p values is given in the Table 6 below; the S_f^o and H_f^o at 298 K are, respectively, 123 cal/mol and 105.3 Kcal/mol (Ritter and Bozzelli, 1994). The function $C_p(T)$ was obtained by fit data from C_p values.

Temperature K	500	600	800	1000	1500
$C_p(\text{cal/mol K})$	83,39	93,94	104,91	110,99	118,95
$\Delta G (\text{Kcal/mol})$	-171,395	-188,656	-227,672	-271,807	-400,131
ϵ	0,999844	0,999452	0,998465	0,999998	0,997189

Those results show that the reaction is practically complete, but it is possible to calculate the reagents concentration in the equilibrium point and to have the minimum residence time by the equation following (Silva, 1996):

$$t = \text{Exp} \left\{ \text{Ln} \left[-\frac{1}{A} \cdot \left(\text{Ln} \frac{C_R}{C_R^o} \right) \right] + \frac{E_A}{R \cdot T} \right\} \quad (11)$$

To have the residence time it is needed confiabile and precise values for E_A and/or Arrenius's factor A for the TCDD molecule, which are being looking for at the moment.

It is known that the cement kilns have good conditions for the co-processing of residues that have dioxins and furans in its composition, since the temperatures observed in them are very high and enough for the destruction of these molecules. But in spite of the great conditions for the dioxins and furan destruction inside the kiln, good conditions can exist for its "de novo" formation in the following stages. The fly ash, particles, and metallic surfaces are good catalyser for the dioxins and furan formation, what happens in places with temperature between 230°C and 400°C. One of the resources used by the cement industry is to promote the fast gas cooling after the exit of the kiln. Also, many processes have aspersion towers of water after their cyclone towers that promote the decrease of the particles concentration in the eletro-filter, they also promote a good gases cooling. The presence of SO_2 in the gases also helps in the emissions control. Most of the fuels used in the cement production, coal or combustibile oil, has considerable rates of sulphur, that when burned forms SO_2 . When the amount of sulphur in the fuel is low, the industry puts CaSO_4 in the raw mix in order to obtain an acid atmosphere inside the kiln, which will promote the concentration reduction of alkaline bases harmful to the operation of the kiln. Normally, this rich atmosphere in Sulphur will also contribute to the decrease in the dioxins and furan formation, according to studies made in pilot scale at the request of USEPA (Gullett and Seeker, 1997). These studies also demonstrate that there is a strong correlation between the emissions of monoxide of carbon and the dioxins and furan emissions. As it is quite difficult and expensive to monitor the dioxins and furan emissions directly, it is rule to do a good combustion control, for the monitoring of the CO emissions and, indirectly, the dioxins and furan control will be also being done. The USA Environmental Technology Council proposed that the limits of CO emissions were established in 100 ppm and of total hydrocarbons (precursors) in 20 ppm in order to staying the emissions levels inside of the limits indicated by USEPA, which is, of 0,12 ng/Nm³ as TEQ Dioxin corrected for 7% of free oxygen. The European norm establishes 0,1 ng/Nm³ for 11% of free oxygen (Richardson, 1995).

CONCLUSION

In a cement kiln, the residues to be co-processed can be introduced together with the main fuel, mixed to him, or placed separated in another part of the process, as it is what happens with used tires that are especially introduced in intermediary followings of the rotative kiln by windows conceived for this, or together with the raw mix that enters in the kiln, a lot of times already heated up. This procedure can cause the formation of vapors contaminated with dioxins and furans that won not be destroyed, since the temperature in that part of the process is smaller than that necessary one for the destruction of these composed, or at least the formation of precursors that will unchain the dioxins and furan synthesis. This danger becomes larger when the kiln used is wet process, where the gases in the exit of the kiln have smaller temperature and there is not the system of pre-heating promote a fast gas cooling.

The residue type being co-processed can also contribute to the dioxins and furan formation. Tires, mass oleaginous, inks waste, refuses from refineries, lignins, wood, plastics, etc. are some of the most common residues found in the co-processing. It can there are residues that contain sources of chlorine, like PVCs, NaCl, HCl, CFCs and other combinations of complex organic structures, atmosphere with chlorine presence (and other halets), strip of appropriate temperature and presence of catalytical ambient, unfortunately will unchain the formation of equivalent of dioxins and furan harmful to the human and animal health.

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