

CASE STUDY CONCERNING MATHEMATICAL MODELLING OF THE EMISSIONS AND THEIR MONITORING WHEN WASTES ARE CO-INCINERATED IN CLINKER KILNS

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În ultimele decenii industria cimentului s-a implicat în coprocesarea deșeurilor rezultate din alte industrii, ca o prioritate în efortul ei în direcția gestiunii responsabile a resurselor neregenerabile.

În timpul coprocesării deșeurilor, conformarea cu cerințele privind emisiile este vitală și în acest sens a fost realizată o modelare matematică a emisiilor de poluanți rezultate la co-incinerarea mai multor combinații de amestecuri de combustibili. De asemenea, au fost organizate o serie de teste în cadrul cărora au fost utilizate mai multe tipuri de combustibili tradiționali și alternativi și a fost monitorizată întreaga gamă de poluanți, cuprinzând pulberi, SO₂, NO_x, CO, HCl, HF, metale grele, dioxine și furani.

Atât modelarea cât și monitorizarea au dovedit faptul că utilizarea combustibililor alternativi în cuptoare rotative de clincher de tipul celui existent la Carpatcement Holding nu conduce la creșterea emisiilor în aer și în toate situațiile emisiile rezultate de la cuptor se situează sub valorile limită stabilite de cerințele legale.

Cement industry has been involved for the last decades in the co-processing of wastes resulting from other industries, as a priority in its effort toward a responsible management of non-renewable resources.

During this process, complying with the legal requirements concerning emissions is vital and in this respect a mathematic modelling of the pollutant emissions resulting from waste co-incineration of different fuel mix combinations was developed. Also more series of tests were performed when different types of traditional and alternative fuels were used and the entire range of pollutants was monitored, including dust, SO₂, NO_x, CO, HCl, HF, heavy metals, dioxins and furans.

The modelling and the monitoring tests proved that use of alternative fuels in the rotary clinker kilns of the type existing in Carpatcement Holding does not lead to increase of air emissions and in all situation the kiln emissions stay within the limit values established by the legal regulations.

Keywords: waste co-incineration, clinker kilns, pollutant emissions

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1. Introduction

Waste co-incineration in the clinker kilns is increasingly used by the cement companies all over the world. Every year bigger and bigger quantities of different types of wastes are recovered in the cement plants: only in the Cembureau* countries the kilns in the cement plants used in 2003, 5.4 million tons of alternative fuels waste derived, but in 2004 the quantity increased to more than 6.1 million tons, representing 17 % substitution of traditional fuels by alternative fuels [1].

The effort in this area is stimulated by the challenges and the priorities identified for the cement industry in the 21st century: “by consuming less energy, fewer natural resources input and generating less pollution per unit of product, we hope to produce more cement complying with the growing requirements of our clients” [2]. The keyword is efficiency: produce more with less; reduce the costs and the impacts related to our production.

2. Co-processing of waste and by-products in the clinker kilns

As part of the actions undertaken for the responsible use of non-renewable resources, special attention has been given by the cement industry for decades to the co-processing of wastes or by-products resulting from other industries or the municipal ones as alternative fuels and alternative raw materials. Figure 1 shows different types of secondary products and wastes and the activities where they are generated.

Waste co-processing presents two aspects in the cement plants:

Energy recovery of the waste having energy content by **co-incineration** (partial substitution of traditional fuels by waste derived alternative fuels) possibly with pre-treatment;

Material recovery of wastes with an adequate chemical and mineralogical content as:

alternative raw materials (partial substitution of the raw materials)

grinding additions (partial substitution of the clinker)

* Cembureau is the European Cement Industry Association including 28 members, industry associations and cement companies of the European Union (with the exception of Cyprus, Malta and Slovakia) plus Norway, Switzerland and Turkey

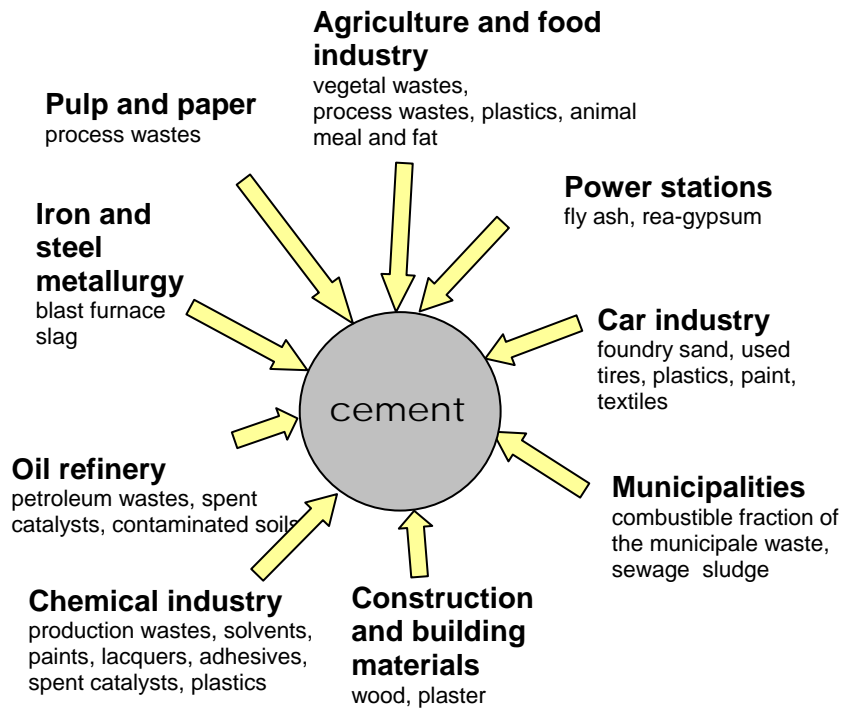


Fig. 1. Types of secondary products and waste materials co-processed in the cement industry and the generating activities

Waste co-incineration is possible in the cement plants because of the specific technological conditions required for the cement production. Figure 2 presents the temperatures range and the gas retention time for a 4 stage cyclone preheater rotary kiln, representing a Best Available Technology.

Co-incineration of a large range of waste types is possible in safe conditions in these types of kilns which present the following advantages [3]:

- very high temperature of the flame (2000⁰C);

- 6 – 8 seconds retention time for the combustion gases at temperatures > 1100 – 1200 ⁰C, leading to the complete destruction of the organic compounds fed into the kiln through the main burner;

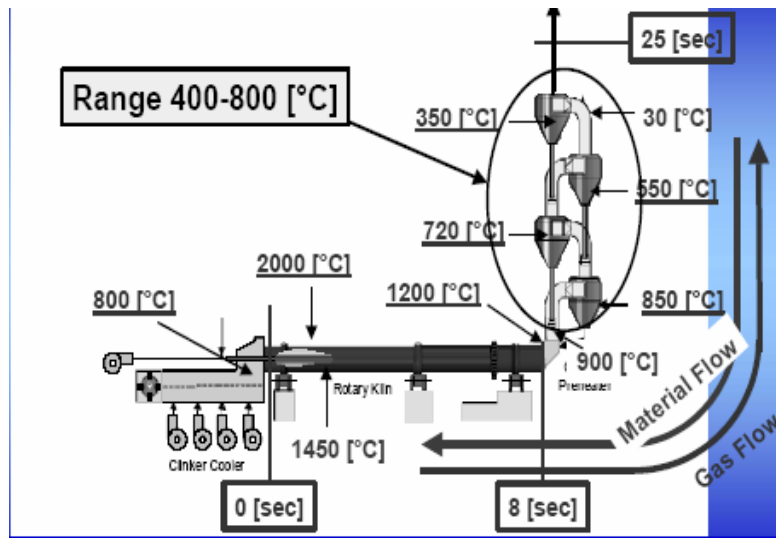


Fig. 2. Temperature range and retention times in the cyclone preheater and in the clinker kiln [K. Karstensen Sintef]

the dimensions as well as the very large quantity of heated material for the modern kilns (at least 3000 t/day) provide a high thermal stability. Even if the clinker kiln stops due to an emergency situation, all hazardous wastes in the kiln are completely destroyed, provided that in this situation the waste feeding is interrupted [4].

excess of O_2 required by the process, therefore complete combustion, implicitly total recovery of the energy value of the wastes;

no other secondary products are generated (slags, ashes) requiring subsequent disposal. The resulted burning secondary products are integrated in the clinker structure, implicitly providing the total recovery of the material value of the wastes;

neutralizing of the exhaust acid gases by the raw materials circulating in a counter-current and having a strong alkaline reaction. The multi-stage suspension preheater of the kiln operates as a scrubber system, highly effective in retaining SO_2 and other pollutants [5].

gaseous emissions resulting from the cement production process – NO_x excepted – are mainly influenced by the quality of the available raw materials and are only to a small extent influenced by the fuels used.

cement production is a closed cycle process where all minerals input in the system – hazardous compounds such as certain heavy metals included – are safely incorporated in the product and are eliminated only to a very small extent in the gaseous emission;

the final product in applications is concrete and mortar acting as a multi-barrier system for metals which are chemically and structurally bound in the hydrating products of the cement;

In spite of the technological advantages of the clinker kilns, the quantities of co-incinerated wastes in the cement plants can not be unlimited. Due to particular care about the product quality, environmental aspects and safety precautions, each type of waste in a specific kiln is a case by case analyse. In such a situation a very useful tool is represented by the mathematical modelling of the pollution resulting from the co-incineration process which offers the possibility to assess the impact before the activity takes place.

3. Emission modelling for waste co-incineration in the clinker kiln of Carpatcement Holding – Deva branch

In order to have an overview of the emissions of pollutants resulting from waste co-incineration in the cement plant Carpatcement Holding SA – Deva and of the impact of these emissions on the neighboring areas, a mathematical modelling was applied, having as result calculation of the likely values of the various emissions in an area of 21.27 km x 23.37 km.

The 8 fuel mix combinations selected for carrying out the mathematical modelling are presented in table 1.

Table 1

Fuel mix combinations and quantities considered in the modelling

Fuel mix		Total alternative fuels input t/h
V1	G+C+SAF+U	13
V2	G+C+SAF+S	13
V3	G+C+ECO-FUEL + U	13
V4	G+C+ECO-FUEL+S	13
V5	P+C+SAF	8
V6	P+C+ECO-FUEL	8
V7	G+P+C+SAF	8
V8	G+P+C+ECO-FUEL	8

Where:

G = natural gas;

P = heavy oil;

C= rubber (old tires);

S = solvents;

U = used oil;

SAF = solid alternative fuel produced from household wastes

ECO-FUEL = alternative solid fuel produced by impregnating sawdust with petroleum wastes, used oil, acid tars, sludges etc.

The mathematical model applied was based on the atmospheric dispersion model for pollutants developed within the US Environmental Protection Agency and using stoichiometric calculi and a combination of the EEA – EMEP – CORINAIR and AP-42 emission factors. The input data included fuels composition, mass flow rate of the flue gases, source location, terrain elevation and average meteorological conditions for the impacted area. Using the model the pollutant emissions (kg/h) and the pollutant concentrations in the combustion gases (mg/m^3) were calculated for all the 8 fuel mix combinations. These values were compared with the limit values prescribed by the legislation in force: OM (Ministerial Order) 462/98 and the HG (Governmental Decision) 128/2002, the transposition of the Directive 2000/76/EC on the incineration of waste.

As a conclusion of the modelling, for each of the fuel mix combination, the emissions of pollutants in the atmosphere are maintained within the acceptable limit values of the current regulations. There are two exceptions, cadmium and thallium emissions for the fuel mix 3 and 4, where, in order to be compliant to the required emission limit values, the quantities of alternative fuels are to be reduced by about 10%, special attention being paid to the used oil and the used solvents. In this situation, the maximum quantity accepted for co-incineration represents maximum 4.5 t/h of each of them.

The concentration values calculated using the model: the yearly average concentrations $C_{\text{yearly average}}$ and the maximum concentrations for 30 min $C_{\text{max 30 min}}$ were compared with the legal regulations concerning the quality of ambient air for SO_2 , NO_x , CO, Cl, halogens (fluorine + bromine + iodine), P, cyanides, PCB/PCT and heavy metals: Be, Z, Sb, As, Cr, Co, Cu, Sn, Mn, Ni, Se, Te, V, Tl, Cd and Hg.

The mathematical model used a post-processor module for plotting the area impacted and curves of isoconcentrations $C_{\text{yearly average}}$ and $C_{\text{max 30 min}}$ were set out for each of these pollutants. As an example, for one of the pollutants, i.e. Pb, these curves are presented in figures 3 and 4.

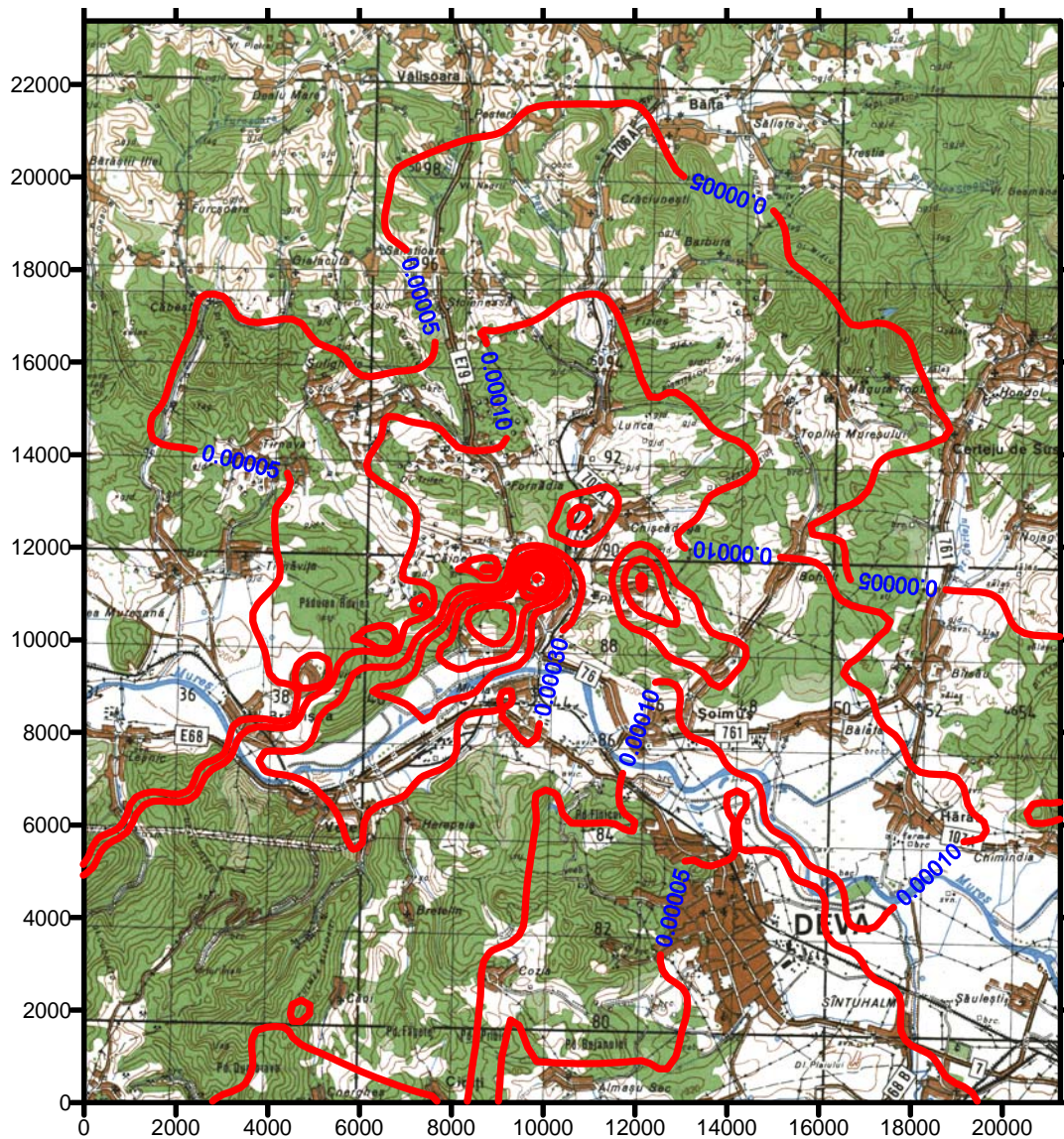


Fig. 3. Yearly average concentration of Pb in the ambient air ($\mu\text{g}/\text{m}^3$) Fuel mix combination V4-V5

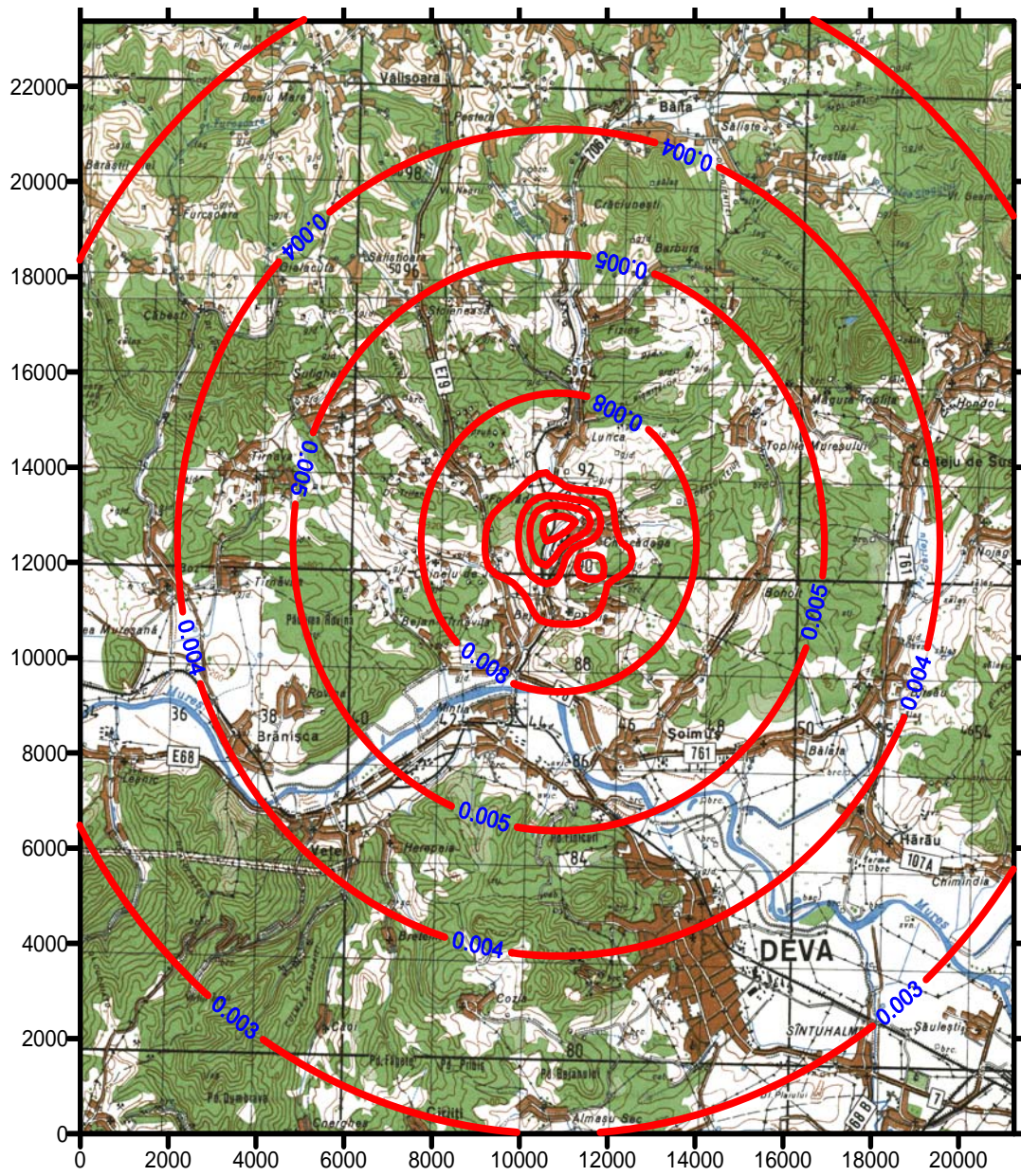


Fig. 4 Maximum concentration of Pb in the ambient air –30 minutes average ($\mu\text{g}/\text{m}^3$) Fuel mix combination V4-V5

4. Emission monitoring for waste co-incineration in the clinker kiln of Carpatcement Holding – Deva branch

Besides the modelling of the pollutants emissions in the case of the kiln using alternative fuels, a full monitoring test was performed for the same kiln. The test program had in view that stack emission measurements should be carried out under stable kiln conditions for the basic fuel (methane gas and heavy oil) and for various substitution percentages of these fuels with old tires and used oil. The parameters to be monitored and the places and type of monitoring are presented in table 2.

Table 2

Parameters and monitoring type

No.	Parameters to be monitored	Place and type of monitoring				
		Supply				Stack
		gas	heavy oil	old tires	used oil	
1	Input (t, m ³)	x	x	x	x	
2	Calorific value			x	x	
3	Temperature and, humidity of the gas					x
4	O ₂ concentration					x
5	Dust concentration					C
6	NO _x (as NO ₂) concentration					C
7	SO ₂ concentration					C
8	CO concentration					C
9	HCl concentration					S
10	HF concentration					S
11	TOC concentration					C
12	Heavy metals concentration					S
13	Dioxins and furans concentration					S

Where:

C = continuous for 24 hours and average for ½ hour

S = spot (average of 3 measurements)

The kiln system is equipped with a 2 lines ESP exhausting gases in the atmosphere through 2 identical stacks (A and B).

Table 3

Results of the measurements

Pollutant	MU	Emission limit values according to 2000/76/EC Directive	Measured values		Measured values		Measured values		Measured values		Measured values	
			A	B	A	B	A	B	A	B	A	B
			Gas + old tires		Gas + old tires + used oil		Gas + old tires + heavy oil		Heavy oil		Gas	
Dust	mg/Nm ³		2.3	3.38	2.57	4.1	3.22	5.37	1.9	3.52		
SO ₂	mg/Nm ³	50*	0	0	0	0	0	1	0	0	1	1
CO	mg/Nm ³	-	345	340	367	363	353	343	269	276	218	238
TOC	mg/Nm ³	10*	8		8.7		7.7		7.9		7.6	
HCl	mg/Nm ³	10	3.5		8.4		5.2		5.4		0.59	
HF	mg/Nm ³	1	0.9		0.65		1		0.95		0.35	
Cd+Tl	mg/Nm ³	0.05	0.0045		0.0043		0.0038		0.0037		0.0096	
Hg	mg/Nm ³	0.05	0.043		0.050		0.03		0.023		0.017	
Sb + As + Pb + Cr + Co + Mn + Ni + V	mg/Nm ³	0.5	0.038		0.038		0.031		0.031		0.0159	
Dioxins and furans	ng/Nm ³	0.1	0.069		0.043		0.032		0.015		0.026	

* contribution of the waste co-incineration

The measurements were carried out by a foreign laboratory accredited in the country of origin, based on the methods of analysis that are ISO standards or standards acknowledged in the EU, using installations and equipment accepted both in the country of origin and by the Romanian Ministry of Environment and Water Management.

The test was conducted in the period 25 – 29.10.2004 as follows:

- a) 25 - 26.10 fuel mix : gas + old tires 3 t/h
- b) 26 – 27.10 fuel mix: gas + old tires 3 t/h + used oil 1.8 t/h, average
- c) 27 - 28.10 fuel mix: gas + heavy oil (30 % gas and 70 % heavy oil) + old tires 3 t/h
- d) 28 – 29.10 : heavy oil

A similar test was conducted on 17.09.2003 when the same set of measurements was carried out by the same laboratory, on the same installation that used as fuel natural gas at that time.

The measuring points were set on a rectilinear part with a length, before and after the measuring points, that exceeds 5 diameters (stack diameter 2.57 m), complying with the provisions of Order 462/1993 on Technical conditions regarding atmosphere protection and of ISO 9096/1992 regarding the dust isokinetic sampling, so that a uniform distribution and no disturbances of the flow of flue gases occurred.

The synthesis of the results of the measurement for each of the 4 fuel mix combinations is presented in table 3.

The concentrations are presented under standard conditions: temperature 273.15 K, pressure 101.325 kPa, dry gas, 10 % O₂.

The concentration of dioxins and furans is expressed as a sum in ng. m⁻³ TEQ (toxic equivalent).

5. Conclusions

The mathematical modelling and also the complete range of emissions monitoring performed at the clinker kiln of Carpatcement Deva branch, proved the fact that using alternative fuels in different fuel mix combinations, brings no supplemental pollution and in all situations the kiln emissions stay within the limit values established by the legal regulations.

LIST OF ACRONIMS

EEA = European Environmental Agency

EMEP = European Monitoring & Evaluation Program

CORINAIR= Emission Inventory Program developed by EEA Task Force

AP-42 = Compilation of Air Pollutant Emission Factors issued by the US Environmental protection Agency (EPA)

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