EMISSIONS FROM CEMENT KILN STACK FEEDING ALTERNATIVE FUELS

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Introduction

The use of solid wastes as supplementary fuel or raw material substituted in cement kilns is one of the best technologies for complete and safe destruction of these wastes, due to the fact that there is a simultaneous benefit of destroying wastes and getting energy. The main benefits in using solids wastes in cement kilns include energy recovery, conservation of non-renewable fuels, reduction in cement production costs and the use of already existing facilities. Types of wastes presently used by the cement industry as supplementary fuel include paint thinners, degreasing solvents, solvents from ink and printing industries, chemical byproducts from pharmaceutical and chemical manufacturing, waste oils, waste tyres, municipal solid wastes, sewage sludge and waste timbers.

At present work, the results of the analysis in the emissions of a cement kiln in different fuel situations are showed. The kiln has been fed with petroleum coke and two wastes: whole tyres and sewage sludge. Six series of sampling were performed in the stack of the factory to analyse the changes in emissions. In the series, the composition of the fuels used to heat the furnace were changed from no sludge used (only coke and tyres) to no tyres used (only coke and sewage sludge).

Dioxins and furans (PCDD/Fs), heavy metals, polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), HF and HCl were analyzed according to standard methods of sampling and determination.

The use of sewage sludge as an alternative fuel has its advantages and drawbacks; among the advantages one can cite that is a cheap fuel that is considered as biomass, and then does not contribute to the total emission of CO_2 considered in the Kyoto protocol. But as a disadvantage, environmental regulations are generally more exigent and there is a necessity to adapt the installations.

Materials and Methods

The wastes used are whole tyres and two different sewage sludge (due to the inability to get the same sludge continuosly) and their characterization are shown in Table 1.

The methods used for sampling and analysis are standard methods suggested by the Spanish regulations for stack analysis. Almost of the sampling methods were carried out in isokinetic conditions with an equipment APEX INSTRUMENTS system, model SK-MM5HS. Specifically, methods used were:

- PCDDs/Fs sampling: EPA Method 0023A, European Norme EN 1948-1 (isokinetic)
- PCDDs/Fs analysis: EPA Method 1613 (HRGC/HRMS with labelled congeners)
- PAHs sampling: EPA Method 0010 (no isokinetic needed)
- PAHs analysis: EPA Method 8100 (mass spectrometry, no high resolution)
- COVs sampling: EPA Methods 0040 & 0031 (with TENAX resin)
- COVs analysis: EPA Method 8260B (thermal desorption with mass spectrometry)
- HCl/HF sampling: EPA Methods 0050 & 0051 (isokinetic)
- HCl/HF analysis: EPA Method 9057 (ionic chromatography)
- Heavy metals sampling and analysis: EPA Methods 0060, 0029, 3051, 3015 (isokinetic sampling, analysis by ICP-MS).

		SEWAGE SLUDGE 1	SEWAGE SLUDGE 2	WASTE TYRES
	Weight loss (105ºC, %)	10.0	7.03	0.9
	Weight loss (550ºC, %)	27.6	31.2	65.5
	NCV (MJ/kg)	16.99	11.77	33.08
	Total chloride (mg/kg)	1804	3890	5023
	Total sulfur (mg/kg)	12408	17820	17106
Metal analysis (mg/kg)	*Cd*	13.4	2.9	-
	Tl	<0.5	0.1	-
	Hg	<0.5	1.2	-
	Sb	4.2	0.15	-
	As	<0.5	2.4	-
	Pb	69	72	-
	Co	1.6	4.5	-
	Cu	217.7	562.3	-
	Cr	178.1	572.7	-
	Mn	128.1	182.2	-
	Ni	35.8	223.2	-
	V	11.3	17.4	-
	Sn	<0.5	55.5	-

Table 1: Characterization of wastes used

In addition, in all the samplings some parameters were continuously monitored: O_2, SO_2, NO_2, NO, CO_2, CO and gas temperature. This is necessary to correct the gas composition to the standard legally established (normalize the O_2 content), and was done by using a portable analyzer made by LAND, model LANCOM 6500.

The cement factory studied has a production of 150 tons/h of clinker. The furnace needs a total of thermal energy close to 3000 MJ/ton. The usual fuel used to get this energetic input is petroleum coke (NCV 37.5 MJ/kg) and waste tyres. The points where fuels are added to the kiln are different according to its nature: whereas the petroleum coke is added in the main burner, the whole tyres are fed at the beginning of the kiln, in the point where cement raw material goes into the kiln. This is due to the cement factory uses a combustion technology equivalent to the combustion by stages to decrease the NO_x emissions. The feed of whole tyres in the beginning of the kiln produce a reducing atmosphere to break down part of the NO_x generated in the sinterization zone[1]. In addition, sewage sludge are also fed in the main burner with petroleum coke. The gas leaving the furnace is mixed with the cement raw material in order to interchange the heat in a multi-cyclone system. Later the gas is passed through an electrostatic precipitator, with a final temperature close to 130 ºC, where the samplings were made.

Six series of runs were carried out, with differents mass flows of sludges and tyres. In each series, the sampling of all the pollutant was done in three different days: one day for metals and VOCs sampling, other for dioxin and PAHs sampling and one third day for HCl/HF. Table 2 presents the amount of the fuels fed to the furnace in each series, and the ratio corresponding to each waste fuel.

SAMPLING SERIES	A	B	C	D	E	F
Petroleum coke (kg/h)	12000	9800	9000	11800	11450	11300
Waste tyres (kg/h)	*4500*	*1500*	*1000*	*500*	*1100*	----
Sewage sludge 1 (kg/h)	----	*1500*	*3000*	*4000*	----	----
Sewage sludge 2 (kg/h)	----	----	----	----	*5200*	*5600*
% weight TYRES	*27*	*12*	*8*	*3*	*6*	*0*
% weight SLUDGE	*0*	*12*	*23*	*25*	*30*	*33*

Table 2: Fuel composition in the six series

Some parameters were continuously monitored in each sampling. Table 3 resumes the average value of these parameters in each sampling series.

SAMPLING SERIES	A	B	C	D	E	F
O2 (%)	11.3	10.5	8.6	10.5	10.3	10.1
SO2 (PPM)	19	48	53	<0.1	1	0.2
NO2 (PPM)	17	24	8	34	31	66
NO (PPM)	461	549	442	712	650	595
CO2 (%)	8.4	8.3	11.1	9.1	5.8	5.6
CO (PPM)	394	387	1096	651	812	648
TEMPERATURE(ºC)	127	128	142	122	132	125

Table 3: Gas parameters

Results and Discussion

The limits established in Spanish regulations for emissions when a cement kiln operates with alternative fuels, are the following: dioxins and furans 0.1 ng I-TEQ/Nm^3, TOCs 10 mg/Nm^3, 0.05 mg/Nm^3 for (Cd+Tl), 0.05 mg/Nm^3 for Hg, 0.5 mg/Nm^3 for Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V, 10 mg/Nm^3 for HCl and 1 mg/Nm^3 for HF. The volume is calculated at 273 K, 101.3 kPa and at 10 % of oxygen; the regulation is different in USA, the values must be calculated with 7 % of oxygen. The results obtained in all the analyses carried out are in Table 4.

SAMPLING SERIES	A	B	C	D	E	F
Dioxins(total pg I-TEQ/Nm^3))	22.1	5.4	7.7	2.1	2.5	1.9
PAHs (mg/Nm3)						
Naphthalene	0.64	0.41	13.0	nd	0.39	0.0094
Acenaphtylene	0.0020	0.0013	nd	0.00010	nd	0.00060
Acenaphtene	nd	nd	nd	nd	nd	nd
Fluorene	nd	0,0016	nd	0.00010	nd	0.00090
Phenanthrene	0.0051	0.0030	nd	0.0017	0.0026	0.0030
Anthracene	nd	nd	nd	nd	nd	0.00010
Fluoranthene	nd	nd	nd	nd	nd	0.00010
Pyrene	nd	nd	nd	nd	nd	0.00010
Benzo(a)anthracene	nd	nd	nd	nd	nd	0.00090
Chrysene	nd	nd	nd	nd	nd	nd
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	Nd
Gases (mg/Nm3)						
Methane	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Ethane	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Volatile (mg/Nm3)						
Benzene	1.17	0.21	0.95	na	0.49	na
Toluene	1.22	0.74	0.84	na	0.53	na
Xylenes	0.61	0.23	0.66	na	0.51	na
Styrene	0.34	0.26	0.22	na	0.15	na
Benzaldehyde	0.17	0.16	0.11	na	0.03	na
Phenol	0.23	0.04	0.09	na	0.02	na
VOCs total	9.40	5.09	7.50	na	5.20	Na
HCl & HF (mg/Nm3)						
HCl	0.96	<0.1	6.96	1.02	4.39	1.29
HF	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metals (mg/Nm3)						
Cd+Tl	0.00045	0.00147	0.0014	na	0.00040	0.00011
Sb+As+Pb+Cr+Cu	0.08990	0.06500	0.09210	na	0.04030	0.09509

Table 4: Result of the analysis in the six series (nd = not detected; na = not analyzed)

All the analyses of PCDD/Fs are under legal limits, something common to other factories in Spain[2]. The higher level of dioxins is obtained, contrary to all prediction, when no sewage sludge is fed. Some papers in literature also reported no increase of emissions of dioxins with the use of an alternative fuel.[2,3]

With regard to VOCs analyses, although the series have levels lower than the legal limits, the production seems to increase when feeding tyres to the cement kiln, but always meeting the environmental standards.

The PAHs analysed are those sixteen designed by the U.S. EPA as priority pollutants, although there are only six of them that are considered as carcinogenic by the WHO ((Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(ah)anthracene, Indeno (1,2,3-cd) pyrene). A detailed study of PAHs emission from various industrial stacks with similar results has been found in literature[4]. In this study, similar levels of PAHs were found in cement factories; the authors indicate that the use of heavy oil as fuel induces the formation of higher 4, 5, 6 and 7-ring aromatics. In the present study, not so heavy hydrocarbons are found, but the fact that VOCs and dioxins increase with the use of tyres seems to agree with the fact that heavy oils (tyre are composed by really heavy oils) increases the emission of aromatics.

The emissions of HCl and HF are lower than the limits permitted. The series C has abnormal results, coinciding with the values showed in Table 2. This situation indicates that the operation conditions of the cement kiln that day was not the usual, and this affected the emissions.

Finally, the metal emissions are lower than legal limits too. The sampling for series C was not executed because sewage sludge 1 run out (the same occur in VOCs analysis)

In conclusion, the conditions of the furnace (very high temperature, close to 1800 ºC, good mixing and excess of oxygen, almost 200 % stoichometric) make the cement kiln factory an ideal place to get a very good combustion to eliminate the organic compounds produced. The amount of organic matter in the cement raw material seems to be the responsible for the possible changes in emissions of organic compounds [5,6]. Furthermore, the alkalinity of the raw material and the clinker cause the control of the acid gases and heavy metals. Because of that the use of wastes as supplementary fuel in cement kiln is one of the best technologies for complete and safe destruction of these wastes, besides recovering energy.

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