

Organic and inorganic pollutants from cement kiln stack feeding alternative fuels

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Abstract

In this work, an analysis of the emission of different pollutants when replacing partially the fuel type used in a cement kiln is done. The wastes used to feed the kiln were tyres and two types of sewage sludge. The increasing mass flow of sludge is between 700 kg h^{-1} and 5500 kg h^{-1} , for a total production of clinker of 150 t h^{-1} , whereas the fed tyres were in the flow range of $500\text{--}1500 \text{ kg h}^{-1}$. Dioxins and furans, polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons, heavy metals, HCl and HF, CO, CO₂, NO_x and other parameters of the stack were analyzed, according to the standard methods of sampling and determination, through more than 1 year in six series: one blank (no sewage sludge) and five more with increasing amount of sludge and/or tyres. The emission of PAHs and dioxins seems to increase with the amount of tyres fed to the kiln, probably due to the fed point used for this waste.

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1. Introduction

Cement is an important binding agent for construction industry and is produced world-wide in large amounts. In 2000, about 323 million tons were processed in Europe (Bundesverband der Deutschen Zementindustrie [1]).

A central process step during the manufacturing of cement is the production of the intermediate product clinker. For this production, inorganic raw materials are calcined at temperatures in the range of $1000\text{--}1500 \text{ }^\circ\text{C}$. In order to reduce the costs of this energy-intensive process, which has a high share in the manufacturing costs of cement, regular fuels like coal, petroleum coke, oil and gas are increasingly substituted by different types of waste.

Co-incineration of wastes to substitute regular fuels started more than 20 years ago with the use of waste oil and used tyres. In the last 10 years, use of alternative fuels in the cement is continuously increasing. The share of secondary fuels in the total use of fuels in cement plants is expected to increase further.

Chemicals emitted from a source into the environment could be directly transmitted to humans through air inhalation. However, these chemicals could also cross-environmental media boundaries, transferring to soils, vegetation, water, biota, etc. Consequently, human health can be also indirectly affected through different pathways such as drinking water or groundwater, skin absorption of the chemicals present in water, intake of contaminated foodstuffs and oral and skin absorption of chemicals from soils. Therefore, for accurate health risk estimation, the chemical concentrations in each of these environmental media must be determined [2].

The use of solid wastes as a supplementary fuel or raw material substitutes 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. Nevertheless, some wastes, such as those containing an important amount of Hg, should be carefully treated in the kiln. At the same time, substituting primary fossil fuels has environmental and economic advantages. 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 waste presently used by the cement industry as a supplementary

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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 sludges and waste timbers. The feeding rates vary from country to country. For example, while in Spain the limit is 15% of the thermal energy required in the kiln, there is no limit in Switzerland. Although they are actually burned, the thermal decomposition of such wastes has not been in some cases studied from a scientific point of view until now.

Tyres in the cement industry can be used as a whole piece or scraped into pieces, depending on the requirements of the installation. Industrial tests indicate that the costs of using approximately 20% shredded tyre as a fuel substitute are similar to those using only petroleum coke.

In an incineration process, some chemicals are emitted as a consequence of the combustion process, and these chemicals could be directly transmitted to humans through air inhalation. However, these chemicals could also cross-environmental media boundaries, transferring to soils, vegetation, water, etc. Consequently, human health can be also indirectly affected through different pathways such as drinking water or groundwater, skin absorption of the chemicals present in water, intake of contaminated foodstuffs and oral and skin absorption of chemicals from soils.

One of the major hazards in the alternative fuels flue gas composition is the heavy metal (HM) content. Not all heavy metals are toxic and not all toxic heavy metals have the same toxicity. Therefore many countries differentiate between different toxicity classes:

- *class I*: Cd, Hg, Tl;
- *class II*: As, Co, Ni, Se, Te;
- *class III*: Pb, Cr, Cu, Pt, V, Sn, Pd, Sb, Mn, Rh.

The HM in class I are the most toxic and harmful, the HM in class III the least ones. The main sources of HM emissions from cement kiln stacks are either raw materials or fuels containing heavy metals. According to the behaviour of the HM in the kiln system, three classes can be distinguished:

- The non- or low-volatile HM (As, Be, Co, Cr, Cu, Mn, Mo, Sb, Se, Te, V and Zn) are incorporated in the clinker to almost 100%, and therefore do practically not appear as emissions. As a general rule the sum of the emissions of all non-volatiles HM of a preheater kiln is always much below 0.1% of the corresponding metal input.
- The semi-volatile HM such as Tl, Pb and Cd are not completely (Pb, Cd) to very little (Tl) incorporated directly in the clinker. The remaining part which is not incorporated in the clinker is expected to be almost completely adsorbed on the surface of the dust particles in the kiln exhaust gas system.
- Volatile HM cannot be efficiently controlled by dedusting of the kiln exhaust gas because a portion of the volatile HM always remains volatile (not attached to dust particles). The most prominent and only example of relevance to the cement industry is mercury (Hg). Hg is suspected to be emitted to a large degree in vaporous form and can be retained by carbon

filters. The lower the exhaust gas temperature is at the filter inlet the higher is the proportion of Hg attached to dust particles that can be removed from the exhaust gas. The origin of Hg is the cement raw material as well as the fuels.

The present work has the main purpose of checking the amounts of pollutants emitted by a cement kiln in different situations. Two different wastes were fed to the kiln, as a part of an industrial project concibed to develop an efficient system to eliminate the wastes. Six series of sampling were performed in the stack of the factory. In the series, the composition of the fuels used to heat the furnace was changed.

Dioxins and furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), heavy metals, HCl, HF and volatile organic compounds (VOCs) are analyzed, according to standard methods of sampling and determination (details later). Tests in the cement kiln were performed through more than 1 year, because of the difficulty of the work done.

Heavy metals entering the kiln (with the fuels and with the raw materials) have three different ways to exit the system: they can exit with the cement clinker, emitted through the stack and can also be found in the filter dust cement. Levels of metals in this last material are surprisingly high [3], arriving at levels close to 300 ppm for As.

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 CO₂ considered in the Kyoto protocol. But as a disadvantage, environmental regulations are generally more exigent and there is a necessity to adapt the installations.

2. Materials and methods

Characterization of the sludges and tyres was carried out. Table 1 shows the details of the analysis performed. Two different sewage sludges were used in the study period, due to the inability to get the same sludge continuously.

The methods used for sampling and analysis are the standard methods suggested by the spanish regulations for stack analysis. Specifically, methods used were

- *PCDDs/Fs sampling*: EPA Method 0023A, European Norme EN 1948-1 (isokinetic).
- *PCDDs/Fs analysis*: EPA Method 1613 (high-resolution gas chromatography coupled to a high-resolution mass spectrometer (HRGC/HRMS) with labelled congeners).
- *PAHs sampling*: EPA Method 0010 (no isokinetic needed).
- *PAHs analysis*: EPA Method 8100 (mass spectrometry, no high resolution).
- *VOCs sampling*: EPA Methods 0040 and 0031 (with TENAX resin).
- *VOCs analysis*: EPA Method 8260B (thermal desorption with mass spectrometry).
- *Heavy metals sampling and analysis*: EPA Methods 0060, 0029, 3051, 3015 (isokinetic sampling, analysis by inductively coupled plasma with a mass spectroscopy (ICP-MS)).

Table 1
Characterization of the sludges and tyres used in the cement kiln

	Sewage sludge 1	Sewage sludge 2	Waste tyres
Weight loss (105 °C, %)	10.0	7.03	0.9
Weight loss (550 °C, %)	27.6	31.2	65.5
NCV (MJ kg ⁻¹)	16.99	11.77	33.08
Total chloride (mg kg ⁻¹)	1804	3890	5023
Total sulfur (mg kg ⁻¹)	12408	17820	17106
Metal analysis (mg kg ⁻¹)			
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	–

- *HCl/HF sampling*: EPA Methods 0050 and 0051 (isokinetic).
- *HCl/HF analysis*: EPA Method 9057 (ionic chromatography).

Almost all these methods have in common the necessity to get an isokinetic regime for gas sampling. The isokinetic sampling equipment was an APEX INSTRUMENTS system, model SK-MM5HS.

PCDD/Fs requires over 8 h of sampling time, and the analysis was carried out by high-resolution gas chromatography coupled to a high-resolution mass spectrometer. An Agilent HP5890 gas chromatograph equipped with a PTV inlet with a septumless head was used. For HRMS, a Micromass Autospec UltimaNT mass spectrometer (Micromass, Waters, U.K.) with a positive electron impact (EI+) source was employed. The analytical procedure comprises the extraction with toluene, change of solvent to hexane and cleanup using the Power Prep system (FMS Inc., MA) with three different columns: silica, alumina and activated carbon (FMS Inc., Boston, U.S.A.). 13C-labelled compounds included in the EPA 1613 method were used.

All the solvents (acetone, dichloromethane, toluene, *n*-hexane and ethyl acetate) for organic trace analysis were purchased from Merck (Germany).

PAHs sampling and extraction is done in the same sample than PCDD/Fs. PAHs are analyzed by low-resolution mass spectrometry (a gas chromatograph Agilent 6890N coupled to a mass spectrometer Agilent 5973N) using deuterated isomers, as explained in other contributions [4,5].

Volatile organic compounds were analyzed in two fractions. First fraction, the incondensable volatile fraction, was collected in a 10-L Tedlar bag, and later analyzed by FID-GC (Shimadzu GC-17A) and TCD-GC (Shimadzu GC-14A). On the other hand, a semi-volatile fraction (benzene, toluene, etc.) was adsorbed in a TENAX resin (20 L of gas) that later was thermally desorbed and analyzed by GC/MS (a GERSTEL TDS-2 thermal desorption

system with an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer).

Heavy metals sampling requires over 5 h of sampling time. Heavy metal sampling train consists of six different impingers that lately are treated to extract the metals, according to standard method. Quantification analysis was carried out by inductively coupled plasma with a mass spectroscopy detector. The equipment is model VGPQ-ExCell by thermo elemental.

HCl/HF sampling requires 2 h of sampling time, and the sampling train consists of four different impingers. The analysis is performed in ionic chromatograph equipment (model DIONEX DX 500).

In addition, in all the samplings some parameters were continuously monitored: O₂, SO₂, NO₂, NO, CO₂, CO and gas temperature. This is necessary to correct the gas composition to the standard legally established, and was done by using a portable analyzer made by LAND, model LANCOM 6500.

2.1. Characteristics of the cement factory studied

The cement factory is located close to our working laboratory, and has a production of 150 t h⁻¹ of clinker. The furnace needs a total of thermal energy close to 3000 MJ t⁻¹. The usual fuel used to get this energetic input is petroleum coke, with an average net calorific value (NCV) close to 37.5 MJ kg⁻¹.

This cement plant consists in a rotary kiln where the flow type between the gas and solid phases is countercurrent. In this way, the phenomena involved in the interaction between these two phases have a major driving strength. It is important to note that 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 waste tyres are fed at the other side, in the point where cement raw material goes into the kiln. In addition, sewage sludge is also fed in the main burner with petroleum coke. 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 [6].

The gas leaving the furnace is mixed with the raw solid 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 °C.

2.2. Operating conditions of the runs

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

As commented previously, some parameters were continuously monitored in each sampling. Table 3 resumes the average value of these parameters in each sampling series. Note that the

Table 2
Mean mass flows of the fuels feed to the furnace in each series

	Sampling series					
	A	B	C	D	E	F
Petroleum coke (kg h ⁻¹)	12000	9800	9000	11800	11450	11300
Waste tyres (kg h ⁻¹)	4500	1500	1000	500	1100	–
Sewage sludge 1 (kg h ⁻¹)	–	1500	3000	4000	–	–
Sewage sludge 2 (kg h ⁻¹)	–	–	–	–	5200	5600
Weight tyres (%)	27	12	8	3	6	0
Weight sludge (%)	0	12	23	25	30	33

levels found in sampling series C is much different than in the others. This will be commented later on.

3. Results and discussion

Spanish legislation considers a maximum emission limits of some of the pollutants studied in the present work. For co-incineration plants, as it is considered a cement kiln when using alternative fuels, the limits are

- 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;
- 1 mg Nm⁻³ for HF.

The normal cubic meter (Nm³) is calculated at 273 K, 101.3 kPa and at 10% of oxygen; the regulation is different in USA, where the values must be calculated with 7% of oxygen.

3.1. Dioxins and furans

Table 4 presents the results on the emission of each of the 17 congeners analyzed, and also on the total amount of dioxins (I-TEQ units). The recovery factor was higher than 80% for all the congeners in all the analysis. The data presented corresponds to the whole sampling (two different fractions are analyzed in each sampling, one for the particulate filter and other for the sample train rinses).

Table 3
Results of the parameters continuously monitored

	Sampling series					
	A	B	C	D	E	F
O ₂ (%)	11.3	10.5	8.6	10.5	10.3	10.1
SO ₂ (ppm)	19	48	53	<0.1	1	0.2
NO ₂ (ppm)	17	24	8	34	31	66
NO (ppm)	461	549	442	712	650	595
CO ₂ (%)	8.4	8.3	11.1	9.1	5.8	5.6
CO (ppm)	394	387	1096	651	812	648
Temperature (°C)	127	128	142	122	132	125

Average value for each series.

As shown in Table 4, all the analysis gave a level of dioxins emitted much lower than that permitted (maximum 0.1 ng I-TEQ Nm⁻³). This is common to other factories in Spain, as reported [7–10]. 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 [8,10].

Wurst and Prey [11] indicate that the material used as a fuel in industrial furnaces is not responsible for the emission of dioxins. The conditions of the furnace (very high temperature, good mixing and excess of oxygen) make the cement kiln factory an ideal place to get a very good combustion. Some paper reported that the amount of organic matter in the cement raw material seems to be responsible for the possible changes in emission of organic compounds [12–15].

The data shown in Table 4 apparently indicate that the total emission of dioxins is increased when using increasing amounts of waste tyres. A multivariate analysis has been performed to check this point. The data for the multivariate analysis were the dioxin analysis obtained in each sampling series, together with the corresponding percentage of tyres and sewage sludge. The analysis is able to explain an 85.5% of the data with only two components. Fig. 1 represents the results for principal component 1 (PC1) and principal component 2 (PC2). The main compounds in each component are

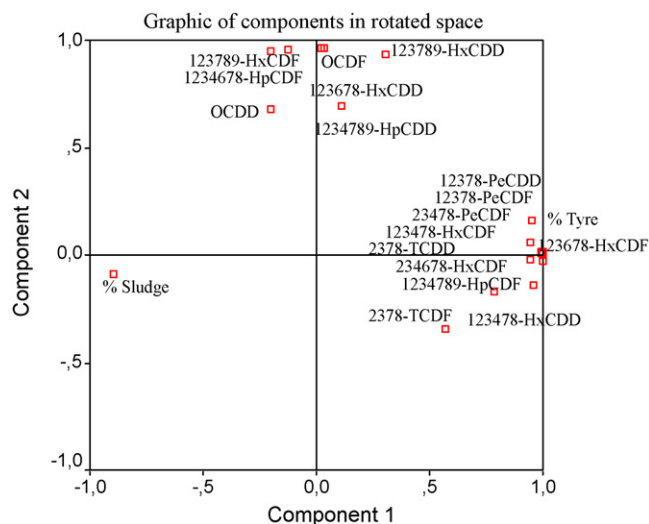


Fig. 1. Principal component analysis for dioxin emissions.

Table 4
Results for dioxins, furans analysis, PAHs, gases, volatiles, heavy metals, HCl and HF

	Sampling series					
	A	B	C	D	E	F
Dioxins and furans (pg Nm⁻³)						
2378-TCDF	13.6	20.5	0.8	0.2	5.0	0.8
12378-PeCDF	4.5	2.4	0.5	0.4	0.5	0.8
23478-PeCDF	17.3	3.5	0.2	1.0	0.9	0.9
123478-HxCDF	26.8	4.3	0.2	0.8	0.5	0.6
123678-HxCDF	14.5	2.3	0.3	1.2	0.4	0.6
234678-HxCDF	18.2	2.9	0.3	1.1	0.6	0.3
123789-HxCDF	4.1	0.1	29.3	0.7	0.8	0.2
1234678-HpCDF	45.5	6.8	157.7	4.1	8.7	0.9
1234789-HpCDF	7.7	2.3	1.2	1.3	1.3	1.1
OCDF	30.5	7.1	210.1	14.5	61.7	2.4
2378-TCDD	1.4	0.1	0.1	nd	0.4	0.8
12378-PeCDD	3.6	0.2	0.1	0.3	0.9	0.5
123478-HxCDD	3.6	0.1	0.2	0.8	0.3	0.3
123678-HxCDD	4.5	0.4	14.5	1.0	0.2	0.3
123789-HxCDD	4.5	0.5	7.3	0.8	0.9	0.4
1234678-HpCDD	25.0	5.0	31.7	35.5	16.8	0.8
OCDD	42.7	13.5	88.9	68.0	91.2	1.8
Dioxins (total I-TEQ)	22.1	5.4	7.7	2.1	2.5	1.9
PAHs (mg Nm⁻³)						
Naphthalene	0.6394	0.407	13.0283	nd	0.3922	0.0094
Acenaphthylene	0.0020	0.0013	nd	0.0001	nd	0.0006
Acenaphthene	nd	nd	nd	nd	nd	nd
Fluorene	nd	0.0016	nd	0.0001	nd	0.0009
Phenanthrene	0.0051	0.0030	nd	0.0017	0.0026	0.0030
Anthracene	nd	nd	nd	nd	nd	0.0001
Fluoranthene	nd	nd	nd	nd	nd	0.0001
Pyrene	nd	nd	nd	nd	nd	0.0001
Benzo(a)anthracene	nd	nd	nd	nd	nd	0.0009
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
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd
Gases (mg Nm⁻³)						
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 Nm⁻³)						
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 and HF (mg Nm⁻³)						
HCl	0.96	<0.1	6.96	na	4.39	1.29
HF	<0.1	<0.1	<0.1	na	<0.1	<0.1
Metals (mg Nm⁻³)						
V	0.0036	0.0062	0.0062	0.00130	0.00196	
Cr	0.0031	nd	0.0016	0.00240	0.00051	
Mn	0.011	0.0177	0.0197	0.00430	0.08546	
Co	0.0033	0.0034	0.0006	0.00030	0.00123	
Ni	0.0045	0.004	0.0041	0.00180	0.00261	
Cu	0.0124	0.0114	0.0167	0.01960	0.00165	
Zn	0.0153	0.0209	0.0071	<0.01	0.32963	
As	0.0012	0.0014	0.0037	0.00090	0.00102	

Table 4 (Continued)

	Sampling series					
	A	B	C	D	E	F
Cd	0.0002	0.0003	0.0002	0.00030	0.00002	
Sn	0.0068	nd	0.0007	0.00090	0.00047	
Sb	0.0004	0.0003	0.0004	0.00170	na	
Tl	0.0003	0.0011	0.0012	0.00010	0.00009	
Pb	0.0504	0.0206	0.0391	0.00800	0.00065	
Hg	<0.005	<0.004	0.0091	0.02500	0.00837	
Cd+ Tl	0.00045	0.00147	0.0014	0.00040	0.00011	
Sb+ As+ Pb+ Cr+ Cu+ Co+ Mn+ Ni+ V	0.08990	0.06500	0.09210	0.04030	0.09509	

nd, not detected; na, not analyzed.

PC1 ≫ PeCDFs, HxCDFs, 1234789-HpCDF, 12378-PeCDD and 123478-HxCDD

PC2 ≫ 123789 HxCDF, 1234678 HpCDF, OCDF, 123678-HxCDD and 123789-HxCDD

As can be seen in Fig. 1, percentage of tyres is grouped with some congeners in the high values of PC1, indicating that the congeners in this component do increase when fed tyres are increased. On the other hand, sewage sludge percentage does not correlate with the dioxin emitted. This effect could be caused by the differences in the feeding point of both materials: tyres are fed at the end of gas trajectory, i.e., the gases produced in the tyre cracking have lower temperature and a very low residence time in the kiln, whereas the sewage sludge is fed in the other side of the furnace, at the point of maximum temperature and permitting a higher residence time of the volatiles produced.

In a study carried out by Hsu and Ling [16], levels of dioxins and furans in the cement did increase when adding tyres to the fuel in a cement kiln. The authors concluded that the dioxin content in the cement became higher when using waste tyres as an auxiliary fuel in a cement kiln, but the dioxin content still met the environmental standards. Abad and Rivera [17] concluded that there are no differences between emissions in a cement kiln feeding or not waste materials as tyres.

Other authors [18] reported a 37% increase in the rate of emission of CO when using a combination between tyres and coal, a 24% increase in SO₂ and a 11% decrease for NO_x. Nevertheless, the authors indicate a decrease of the rate of emission of organic compounds that is 45% for dioxins and furans. The reason for the differences found respect to the present work should be the different configuration of the cement plant. Mokrzycki et al. [19] reported an increase in emissions only if the alternative fuel is fed to the furnace inlet, i.e., the fuel must be fed to the main burner of the furnace, supporting the conclusions of the present work.

From the obtained levels of emission of the different congeners, it can be calculated an average number of chlorides contained in the dioxins and furans molecules with the following equation:

$$\text{Average number of chlorides} = \frac{\sum_{\text{all the congeners}} y_c n_c}{\sum_{\text{all the congeners}} y_c}$$

where y_c represents the yield (emission) of each congener, and n_c the number of chlorides of the congeners. Fig. 2 shows the average number of chlorides for dioxins and furans obtained from the data presented in Table 4. As it could be seen, there is a trend to decrease both dioxins and furans number of chlorides when decreasing the amount of tyres and/or increasing the amount of sludge fed to the furnace.

3.2. Polycyclic aromatic hydrocarbons

The PAHs analyzed are those 16 designed by the U.S. EPA as priority pollutants, although there are only 6 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 and indeno (1,2,3-*cd*) pyrene). The results are shown in Table 4.

A detailed study of PAH emission from various industrial stacks has been done by Hsi-Hsien et al. (1998). 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 4–7-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

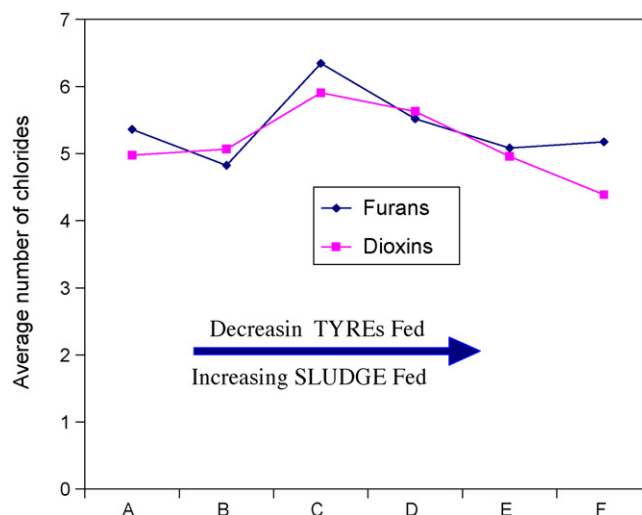


Fig. 2. Evolution of average number of chlorides.

the fact that heavy oils (tyre are composed by really heavy oils) increases the emission of aromatics.

3.3. Volatile organic compounds

Table 4 also presents the results on volatile analysis (two samples were taken as commented above). The legal limit is fixed at 10 mg Nm⁻³. In any case the legal limit is not reached. The trend observed with the production of dioxins is also observed in the VOCs data, i.e., the VOCs production seems to increase when feeding tyres to the cement kiln, but always meeting the legal limits.

3.4. Hydrogen chloride and fluoride

Table 4 resumes the results on HCl and HF emission. All values found are lower than those permitted by Spanish laws. It is worth to note that in sampling series “C” the value found for HCl is much higher than the obtained in the other series. This situation coincides with the abnormal situation of values monitored continuously and shown in Table 3. This indicates that the conditions of the cement kiln were abnormal in this specific day, producing a change in the working conditions that also affected the emissions. It is worth to note that the temperature of the stack gas in this situation was slightly higher than in other situations, indicating that the gas coming from the kiln did not contact with the raw materials as efficiently as usual.

3.5. Heavy metals

Table 4 also resumes the data for metal emission results. The data presented corresponds to the whole sampling (four different fractions are analyzed in each sampling, following the EPA method). The sum of some metals is indicated, specifically of those groups marked by Spanish legislation. Data for metal emission corroborates that in any case the legal limits are not reached. Fig. 3 shows in a more visual way the levels obtained.

The data shown in Table 4 apparently indicate that the emission of some metals increased when using increasing amounts

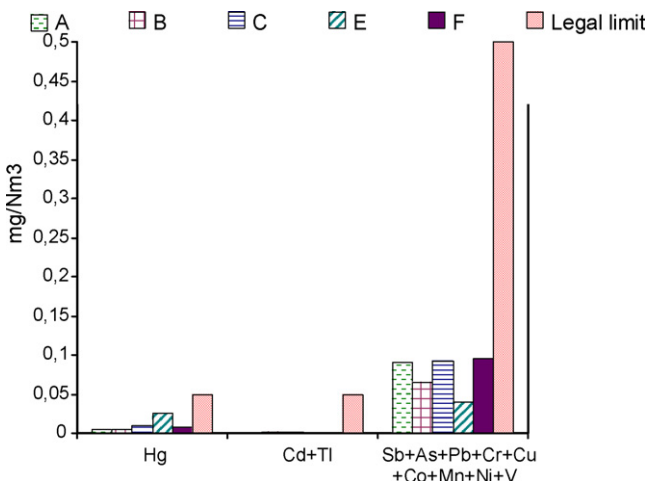


Fig. 3. Metal emissions compared to the legal limit.

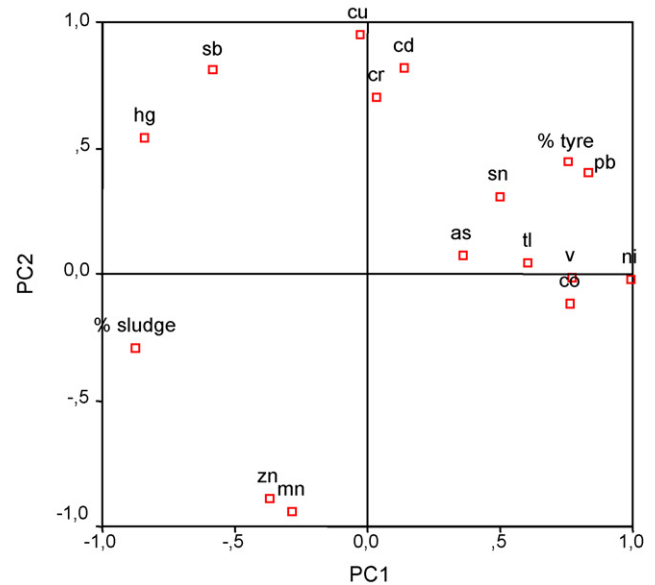


Fig. 4. Principal component analysis for heavy metal emissions.

of waste tyres. In order to find more evidences of similarities and differences between the experiments a multivariate analysis was also performed for HM emissions. The different concentrations of metals obtained in each sampling series, together with the corresponding percentage of tyres and sewage sludge were subjected to a principal component analysis. The results of the PC analysis are shown in Fig. 4. The first PC (41.5% of variance) is positively correlated with concentrations of V, Co, Ni, Pb and with the %tyre in the cement kiln. The second PC (29.9% of variance) is correlated with yields of Cr, Cu and Cd. Fig. 4 presents the PC1 vs. PC2 and the position of the experimental variables. The fact that %tyre is sited close to yields of V, Co, Ni and Pb indicates that these variables have a similar behaviour, i.e., probably the increase/decrease of %tyre means a increase/decrease of these metal yields.

As can be seen, multivariate analysis indicates that the percentage of tyres is grouped with some metals in the high values of PC1, indicating that the metals in this component do increase when fed tyres are increased. All metals in this component pertain to classes II and III of HM attending to their toxicity. Metals on class I (as is the case of Hg) seem not to increase with the increase in tyres ratio. On the other hand, sewage sludge percentage does not correlate with the metals emitted.

Nickel and lead (metals correlated with PC1) are present in tyres, and the data shows an increase of such metals in the stack when feeding tyres. Nevertheless, metals contained in the sludges (Cu, Cr, Mn, Ni and V) does not seem to increase their concentration when increasing the amount of sludges. There are also some metals, such as mercury (Hg) and antimony (Sb) that have a very different behaviours respect to the other heavy metals. The global effect on each metal would depend on its volatility and on the specific amounts contained in tyres and in sewage sludges. The effect found be also motivated by the differences in the feeding point of both materials: tyres are fed at the end of gas trajectory, i.e., the metals contained in the tyres

that are volatilized in the kiln have lower residence time in the kiln to be absorbed by the cement, whereas the sewage sludge is fed in the other side of the furnace, at the point of maximum temperature and permitting a higher residence time of the volatiles produced.

Achternbosch and Braeutigam [3] are more concerned about the quality of the cement itself when using alternative fuels. They find an increase of the trace element concentration of cement due to the use of waste as an input material for antimony, cadmium and zinc. Also lead and cobalt concentrations increase in the cement, but this increase is less pronounced. The authors indicate that contrary to trace elements from raw materials, trace elements from fuels experience an additional resistance in the heat exchanger/rotary kiln system, as a result of which their probability of entering emission is much smaller.

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