PRELIMINARY STUDY OF THE INTERACTION BETWEEN POLLUTANTS AND CEMENT RAW MATERIALPRELIMINARY STUDY OF THE INTERACTION BETWEEN POLLUTANTS AND CEMENT RAW MATERIAL

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Introduction

Sewage sludge is produced in large amounts in all waste water treatment plants. The average production of dehydrated sludge is around 0.2-0.3 kg/(inhabitant. day). In Spain the production of sludge in 1992 was 350000 t dry matter/year, and with a growth prevision to 600000 t dray matter/year for the year 2005. In the European Union, the estimated production of sludge for the year 2005 is around 8-10 Mt dry matter/year ([1]).

The different alternatives for the treatment of these large amounts are compost manufacture, disposal in landfills, pyrolysis and combustion or incineration.

Pyrolysis is one of the alternatives for the treatment of sewage sludge. Some papers can be found considering the formation of gases and volatiles, liquid fuel and char with different adsorption properties. A wide revision of the different authors and specific aspects considered can be found elsewhere ([2]).

On the other hand, the combustion of sewage sludge was also studied for different purposes, discussing the possible stages, operating conditions, types of reactor and formation of toxic by-products. Details of the different aspects can also be found (2). Different aspects of sewage sludge combustion, considering alternative technologies, combustion of volatiles and emission of pollutants was recently reviewed by of Wether and Ogada ([3]).

The use of sewage sludges by the cement industry as a co-fuel is considered useful, where the kiln offers good conditions for complete combustion in terms of temperature and residence time in the kiln. Substituting primary solid fossil fuels has moreover environmental and economic advantages ([4]) due to the sewage sludge is safely eliminated, and also the use of waste as a co-fuel.

Cement kilns are being more and more used to eliminate sewage sludges and other wastes from municipal and industrial waste water treatment plants. In this work, the possible effect of the presence of cement raw material (CRM) during the decomposition of the sludge is investigated in relation to the formation of dioxin, furans and other pollutants.

Methods and Materials

2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF
2.56	1.23	1.75	1.79	1.05	1.17	0.38	21.73	1.11
2.55	1.2	1.78	1.95	1.16	1.25	0.45	22.87	1.21
3.16	1.32	2.19	2.62	1.79	1.83	0.54	26.09	1.42
OCDF	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	Total I-TEQ
75.78	nd	1.59	0.56	6.55	2.87	90.85	745.19	4.57
91.31	nd	1.49	0.39	2.59	1.04	56.33	549.1	3.77
146.17	nd	2.43	0.92	3.5	2.35	68.39	725.47	5.27

The material employed (sewage sludge) was obtained from a municipal waste water treatment plant located in the University vicinity. The ultimate analysis of the sample has been performed in a Carlo Erba Instrument model CHNS-O EA110 and shows a 39 % C, 5.9 % H and 2.8 % N. Chlorine and sulphur content was measured by ionic chromatography, giving a total of 0.18 and 1.24 % respectively. The heating value has been measured in a calorimetric bomb, and has a value of 4059 kcal/kg. The sludge was also analysed for the determination of toxic dioxins and furans. The analysis was triplicated according to the EPA's 1613 method, obtaining the following results (pg/g, total in pg I-TEQ/g):

Combustion runs performed in the present work were conducted in a horizontal reactor which scheme is found elsewhere [5]. The nominal temperature of the runs was in all the runs 850 ºC. In each experiment, 0.1 to 0.2 g of sewage waste was placed in the sample holder and combusted by introducing the sample holder inside the furnace at 1 mm/s. After passing through the furnace, the reactor gas was collected in an adsorptive trap. After each experiment, the adsorptive trap was extracted and the extract was analyzed using different GC-MS techniques, as this study involves analysis of several different classes of compounds. The HRGC-HRMS analyses were performed on an Autospec NT apparatus. The spectrometer was operated in the electron impact ionization at 10000 resolving power. For PCDD/F analysis, 13C-labeled PCDD/F standards (Wellinglon Labs, Canada) were used. Quantitative determination was performed by the isotope dilution method based on the relative response factors previously obtained from three standard solutions (EPA1613-CS1, CS2 and CS3).

Before the trap containing the XAD resin, a modulus containing different materials was placed, in order to study the interaction between the evolved gas and these materials. Materials used comprises cement raw material (CRM), quartz wool, V_2O_5 and/or silica. The very small diameter of the CRM particles made very difficult to pass the gases through a bed formed only by CRM, and a mixture with quartz wool was used; nevertheless, some runs where finally carried out with only CRM. The procedure is similar to that presented before ([5]).

Cement raw material, mainly formed by limestone, shale, silica, and pyrite, is proved to act as a basic matrix where acidic compounds as dioxins/furans should be retained. On the other hand, vanadium is being used as catalyst for the oxidation of volatile organic compounds ([6]). CRM was analysed for dioxin content, giving a total of 0.47 pg/g I-TEQ.

Results and Discussion

The following table resumes the runs performed and the results obtained in the dioxin and furan analysis (all yields in pg/gram of sludge used in the run). In all the runs the percentage of recovery of labeled compounds was higher than 80 %. Each experiment has a code indicating the materials present at the end of the reactor but before the adsorptive XAD resin. As could be seen, some runs were repeated once or twice to corroborate the results.

In order to normalize the results, a multivariate analysis (PCA) of the data was done to statistically evaluate the changes of the profiles and amount of the different congeners. PCA provided a single two-dimensional model, which would explain 76.2 % of the variance in the data. The first PC is correlated to HxCDF y PeCDF. The scatter plot of the component scores on both PC in this first case is presented in Figure 1. As can be seen, runs performed with only sewage sludge are quite different from the others, and a PCA was done without these two experiments. The variance explained in this case is 75.05 %. PC1 is mainly correlated with increasing amounts of 123789-HxCDF and 23478-PeCDF, whereas PC2 is mainly correlated with OCDF and OCDD. Figure 2 presents the results of the second case.

Conditions of reactor exit	No interaction, just sewage sludge	No interaction, just sewage sludge	Quartz wool	Quartz wool	Quartz wool	Quartz wool
CODE	SL1	SL2	QW1	QW2	QW3	QW4
2378-TCDF	n.d.	n.d.	n.d.	n.d.	23.902	n.d.
12378-PeCDF	76.744	134.546	n.d.	14.812	5.920	25.277
23478-PeCDF	2819.800	2307.012	84.448	68.885	62.173	51.584
123478-HxCDF	1876.449	827.318	16.417	20.994	10.807	53.316
123678-HxCDF	587.328	319.366	20.525	29.965	n.d.	36.320
234678-HxCDF	1352.072	1343.682	68.191	40.538	5.661	15.813
123789-HxCDF	408.572	593.241	30.951	20.938	n.d.	16.187
1234678-HpCDF	3821.239	2890.747	212.288	168.552	81.381	103.146
1234789-HpCDF	274.234	283.509	56.901	n.d.	n.d.	381.364
OCDF	742.377	850.641	803.467	1028.792	154.010	81.709
2378-TCDD	n.d.	8.007	n.d.	n.d.	n.d.	n.d.
12378-PeCDD	16.279	32.709	n.d.	n.d.	6.807	43.288
123478-HxCDD	15.677	26.072	15.105	n.d.	n.d.	18.627
123678-HxCDD	9.966	8.766	n.d.	n.d.	6.873	11.165
123789-HxCDD	30.162	15.200	n.d.	n.d.	n.d.	18.601
1234678-HpCDD	364.847	595.718	157.271	179.587	23.391	42.068
OCDD	462.538	821.739	212.790	431.237	25.592	62.519

Conditions of reactor exit	Quartz wool+CRM	Quartz wool+CRM	Quartz wool+CRM	CRM	Quartz wool + Silica	Quartz wool + V2O5
CODE	QW+CRM1	QW+CRM2	QW+CRM3	CRM	QW+SI	QW+VA
2378-TCDF	4.222	3.732	3.160	n.d.	12.127	n.d.
12378-PeCDF	9.175	7.725	11.821	36.448	14.266	8.195
23478-PeCDF	6.390	11.934	20.687	640.352	29.062	7.868
123478-HxCDF	6.061	7.072	35.338	93.929	9.521	7.532
123678-HxCDF	4.480	8.613	11.280	90.414	19.386	n.d.
234678-HxCDF	n.d.	6.317	14.306	211.661	8.664	n.d.
123789-HxCDF	15.449	3.650	28.096	108.056	7.631	8.658
1234678-HpCDF	6.898	n.d.	30.490	347.907	6.196	2.682
1234789-HpCDF	16.511	6.895	26.387	70.667	12.347	4.845
OCDF	n.d.	n.d.	13.615	170.261	n.d.	17.139
2378-TCDD	n.d.	n.d.	14.791	n.d.	7.381	5.130
12378-PeCDD	n.d.	5.539	30.673	n.d.	6.891	9.987
123478-HxCDD	n.d.	9.033	16.208	30.702	6.611	10.353
123678-HxCDD	n.d.	7.362	13.825	46.543	9.424	12.595
123789-HxCDD	n.d.	5.517	17.121	n.d.	20.391	7.800
1234678-HpCDD	n.d.	15.617	41.926	n.d.	14.701	15.832
OCDD	n.d.	35.609	50.290	n.d.	33.661	111.919

Figure 2 shows four zones, where the different runs are sited:

1) Low values of PC1 represent runs with quartz wool present., whereas high PC1 represent no presence of quartz wool. This means that quartz wool influences the yield of 123789-HxCDF and 23478-PeCDF (congeners that contribute to PC1).

2) High values of PC2 represent runs with no CRM present, and a low PC2 correlates with the runs carried out in presence of CRM. This would suggest that the presence of CRM diminishes effectively the amount of octa-chlorinated congeners produced, but is not so effective with other species.

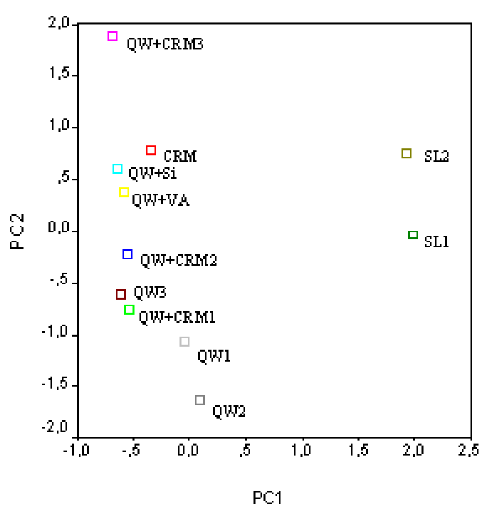

Figure 1. PC2 vs. PC1 (case 1)

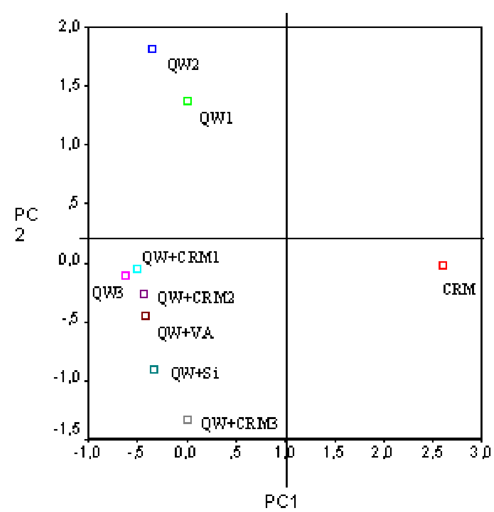

Figure 2. PC2 vs. PC1 (case 2)

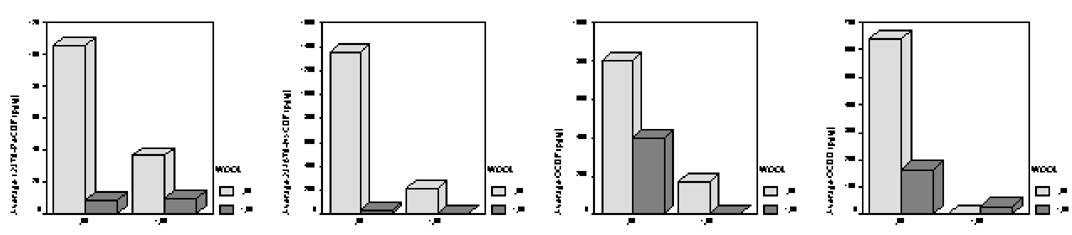
Figure 3. Dioxins/furans retention

Different graphs showing the average yields of each species in presence/absence of CRM and/or quartz wool has also been done. The most important ones are shown in Figure 3. Four averages are presented in each graph: wool=0 is not quartz wool present, wool=1 indicates quartz wool present, CRM=0 is not cement raw material present, and CRM=1 indicates its presence. As could be seen, the presence of quartz wool diminishes the different yields, but the presence of CRM works over the yields, decreasing them more effectively.

Acknowledgements

Support for this work was provided by CYCIT-Spain, Research projectS PPQ2002-00567, PPQ2002-10548-E, and Generalitat Valenciana (Research Group 03090).

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