

Effect of COSMOS technologies in detoxifying municipal solid waste incineration fly ash, preliminary results

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Abstract. This study investigates the effect of technologies for heavy metal stabilization on the concentration of PolyChlorinatedDibenzo-p-Dioxins (PCDD) and PolyChlorinatedDibenzoFurans (PCDF), abbreviated PCDD/F, in Municipal Solid Waste Incineration (MSWI) fly ash. We determined the variation of the Total Organic Carbon (TOC) and PCDD/F concentration between raw and stabilized material. The technologies, that already proved to be very promising for heavy metal entrapment, showed encouraging results also for PCDD/F detoxification. This result could be very impacting on the management of MSWI fly ash: at the best of our knowledge, there are no methods, in literature, that can provide good results in stabilization of heavy metals, and abatement of chlorinated organic pollutants contained in the same matrix.

1. Introduction

It is well known that organochlorinated micropollutants form in traces in thermal processes, such as waste incineration, iron ore sintering, secondary ferrous and non-ferrous smelters, power plants [1-3]. Municipal solid waste presents an heterogeneous composition, containing also hazardous household waste (as plastic bags, paints, chlorine- and metal-containing substances, discarded electronic waste, etc.), that can be problematic when combined with poor combustion conditions, resulting in significant levels of flue gas contamination [4]. As a consequence Municipal Solid Waste Incinerator (MSWI) fly ash, resulting from the treatment of exhaust fume emissions, is an extremely complex material that includes soluble salts, heavy metals, and organic contaminants such as PolyChlorinated Dibenzo-p-Dioxins (PCDD) and PolyChlorinated DibenzoFurans (PCDF), abbreviated PCDD/F [5]. Consequently, MSWI fly ash is considered a hazardous solid waste and its reuse is limited. To improve its environmental characteristics and enhance the possibility of its recovery, it is necessary to develop an effective and economic treatment technology to stabilize or remove hazardous components.

At the University of Brescia two processes for the stabilization of metals in MSWI fly ash, based on the use of silica, were developed: COSMOS process, which uses colloidal silica (Colloidal Silica Mean to Obtain Safe inert, [6-7]), and COSMOS-RICE process, which uses rice husk ash as silica source (Colloidal Silica Medium, to Obtain Safe inert, from RICE husk ash, [8-9]). Both processes obtained good results in terms of metals stabilization.



In the present work our attention was focused on organic contaminants in MSWI fly ash. In particular, we determined the Total Organic Carbon (TOC) and PCDD/F concentration in raw fly ash as well as in the material stabilized with COSMOS or COMOS-RICE treatment. The PCDD/F data were expressed as concentration, ng/kg, or in terms of equivalent toxicity, ng I-TEQ/kg (NATO/CCMS, 1988). This paper presents the preliminary results to evaluate the effect of these mild and sustainable technologies in terms of PCDD/F reduction.

2. Materials and methods

2.1. Samples

MSWI fly ash was collected at fabric filters hoppers of a MSWI plant located in Northern Italy in two different periods: 2008 (FA1) and 2013 (FA2). Flue gas desulfurization fly ash (FGD_FA) and coal fly ash (C_FA) were collected at a power generation plant located in Northern Italy. Rice Husk Ash (RHA) was collected from the particulate collection equipment at the stacks of rice husk-fired boilers. Colloidal silica precursors (Ludox SM-30, Grace Italy) are aqueous colloidal dispersions of SiO₂ particles [6]. An extensive characterization of FA1 and FA2 was already reported [6,8].

Two fly ash mixtures, FA_mix1 and FA_mix2, were prepared mixing three ashes (FA1 or FA2, FGD_FA and C_FA in the respective weight percent: 65%, 20% and 15%). The two mixtures were stabilized by the COSMOS procedure, the obtained samples were named C_mix1 and C_mix2. FA_mix2 was also stabilized by direct use of RHA (COSMOS Rice procedure), and the resulting sample was named CR_mix2.

2.2. Analytical procedures

The TOC content of the samples was determined via three replicate analyses using a TOC analyser (Dohrmann, Apollo 9000) equipped with the standard module (DC-90), the purgeable organics module (PRG-1), and the sludge sediment sampler accessory (S/SS). Details of the analytical method were previously reported [10]. The variability of the TOC data, expressed as percentage standard deviation, was between 2 and 10.

To determine the PCDD/F concentration, the samples were extracted and purified according to the EN 1948-2/3: 2006 method. The obtained extracts were analysed using a VARIAN CP_3800 high resolution gas chromatograph (Dioxin 2 60 m × 0.25 μm Restek capillary column) coupled to a VARIAN 320_MS triple quadrupole mass spectrometer using the tandem mass (MS-MS) operation mode. The 17 toxic 2, 3, 7, 8-congeners (PCDD₂₃₇₈ and PCDF₂₃₇₈) and the tetra- to hepta-homologues non-2378 substituted (PCDD_{non} and PCDF_{non}) were detected and quantified. To evaluate the repeatability of the complete PCDD/F determination procedure, duplicate analyses were performed for each sample: the variation was less than 5%. The lowest operational detection limit (LOD) was found by injecting the most dilute PCDD/F calibration solution (CS1 purchased at Wellington Laboratories Inc.). The LOD was calculated for each homologue group: TCDD and TCDF, 0.04 ng/kg; PeCDD, PeCDF, HxCDD and HxCDF, 0.08 ng/kg; HpCDD, HpCDF, OCDD and OCDF, 0.16 ng/kg.

3. Results and discussion

The effect of silica on heavy metal stabilization was already reported and discussed [6-9]. To evaluate the influence of the stabilization process on organic compounds concentration, the TOC content was determined in all the matrices (Table 1). FA1 and FA2 have a similar TOC content (33691 ppm and 34416 ppm respectively), whereas TOC content is equal to 9092 ppm for FGD_FA and 150732 ppm for C_FA. These matrices were mixed to obtain the materials afterwards stabilized. On the basis of the percentage contribution of FA1 or FA2, FGD_FA and C_FA, the theoretical TOC concentrations for FA_mix1 and FA_mix2 were equal to 46327 ppm and 46799 ppm, respectively (Table 2). After the stabilization with COSMOS process, the experimental TOC concentration were 47871 and 49029 (Table 2), with percentage variation of 3.3% and 4.8% in C_mix1 and C_mix2 with respect to the theoretical ones. These variations are close to the experimental error. To assess the

percentage variation of TOC after the stabilization using COSMOS-RICE process, it is necessary to consider the contribution of RHA to the organic substance (TOC concentration equal to 81591 ppm). On this basis, it is possible to explain the high TOC percentage variation between FA_mix2 and CR_mix2. Based on these results we concluded that the stabilization processes do not influence the total organic carbon concentration in the matrices. Afterwards, PCDD/F were analysed in all the matrices (Tables 1 and 2). The PCDD/F concentration in FA_mix1 and FA_mix2 was calculated on the basis of PCDD/F concentration in FA1, FA2, FGD_FA and C_FA as explained before.

Table 1. TOC, PCDD, and PCDF concentration in raw matrices.

	FA1	FA2	FGD_FA	C_FA	RHA
TOC (ppm)	33691	34416	9092	150732	81591
Σ PCDD ₂₃₇₈ (ng/kg)	6755	21720	11	7	27
Σ PCDD _{non} (ng/kg)	4391	8377	2	< LOD	139
Σ PCDF ₂₃₇₈ (ng/kg)	3868	13844	9	27	4
Σ PCDF _{non} (ng/kg)	9639	20034	26	20	22

Table 2. TOC, PCDD, and PCDF concentration in mixtures and treated matrices.

	FA_mix1	FA_mix2	C_mix1	C_mix2	CR_mix2
TOC (ppm)	46327	46799	47871	49029	57714
Σ PCDD ₂₃₇₈ (ng/kg)	4394	14121	1325	12978	9969
Σ PCDD _{non} (ng/kg)	2854	5445	1405	5058	4254
Σ PCDF ₂₃₇₈ (ng/kg)	2520	9004	1197	8092	6763
Σ PCDF _{non} (ng/kg)	6274	13030	3037	12269	9905

Observing the results obtained, C_FA, FGD_FA and RHA materials were found to contain a very low concentration of total PCDD/F (PCDD/F_{tot}, sum of PCDD/F₂₃₇₈ and PCDD/F_{non}), almost two orders of magnitude lower than the concentrations found in FA1 and FA2. Moreover, the PCDD/F_{tot} concentration in FA2 is two times greater than the concentration found in FA1. The difference in concentration is probably due to the different composition of the waste burned, considering that the two fly ashes were sampled within a temporal interval of five years.

Starting from the data in Table 2, the percentage reductions of PCDD₂₃₇₈ in the samples C_mix1, CR_mix2, and C_mix2 were 69%, 29% and, 8% respectively, corresponding to a detoxification (percentage reduction of the toxicological potential of the mixture expressed as ng I-TEQ/kg) of 51%, 25% and 14%, respectively. For PCDF₂₃₇₈ the percentage reductions in the samples C_mix1, CR_mix2 and C_mix2 were 52%, 25% and, 10% respectively, corresponding to a detoxification of 51%, 24% and, 10% in the same samples.

To point out the efficacy of the treatment, Fig. 1 reports the experimental concentration of PCDD/F in stabilized materials plotted against the theoretical ones for each congener and homologue group, calculated taking into account the dilution due to the addition of the materials used in the process (FGD_FA, C_FA, colloidal silica and RHA). The ideal line at 45° (not indicated in the Figure) corresponds to coincident theoretical and experimental concentration of PCDD/F. This ideal line is almost coincident with the C_mix2 sample, whose reduction of organic contaminants is very low (few percent).

For the samples C_mix1 and CR_mix2, the percentage reduction of the organochlorinated pollutants is greater than the dilution factor (slope of interpolation line less than 1 in Figure 1). In particular, for sample C_mix1, the reduction is about 60% and for sample CR_mix2 it is about 15%. The stabilization processes do not influence the TOC concentration in the matrix as explained before, whereas PCDD/F concentration variation before and after the stabilization process is greater than the

dilution factors. We can suppose, on the basis of our results and previous studies [11], that dehalogenation of organohalogen compounds occurs. Further investigations are needed to verify this hypothesis.

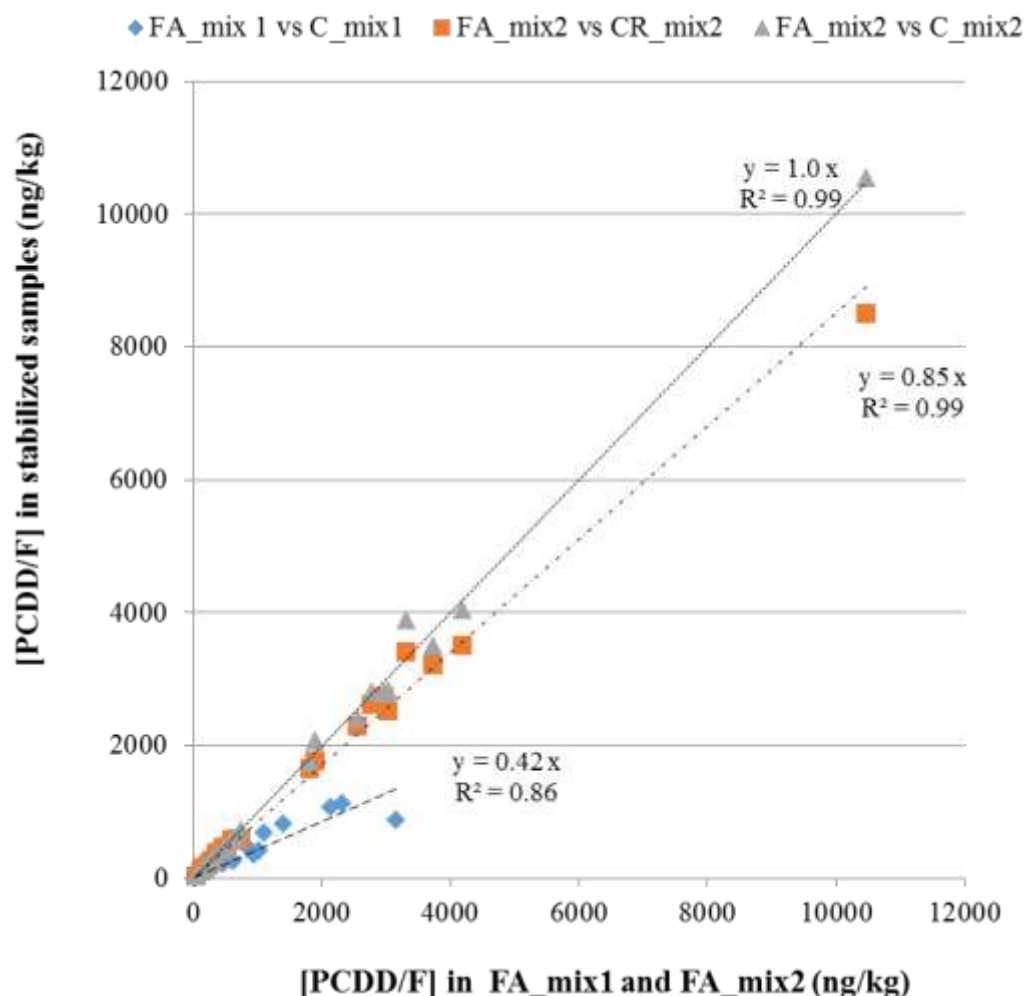


Figure 1. PCDD/F concentration in FA_mix1 and FA_mix2 and the corresponding stabilized material after the treatment with COSMOS and COSMOS-RICE technologies.

4. Conclusion

On the basis of these preliminary results, the COSMOS and COSMOS-RICE technologies, very promising for heavy metal entrapment, proved to be useful also for chlorinated organics reduction. Moreover, these processes are sustainable, as they take place under mild conditions, and all the required reagents are waste materials, except colloidal silica in COSMOS process. This result could be very impacting on the management of the MSWI fly ash: to the best of our knowledge, there are no methods, in literature, that can provide good results not only in salt recovery and stabilization of heavy metals, but also in the abatement of chlorinated organic pollutants contained in the same matrix.

In the next future, the hypothesis of dechlorination taking place during the treatment will be studied in more detail, investigating the role of the reagents, such as colloidal silica, and parameters as the reaction temperature.

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