On the characterization and control of trace heavy metals in the submicron range aerosol from a MSWI boiler.

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The final aim of this work is to reduce the environmental emissions from a municipal sewage sludge incineration line [MSWI] by the development, implementation and systematic application of the concepts, instrumental techniques and paradigms of the aerosol science and technology. Therefore, it is focused in a systematic approach to further optimize the off-gas line according to the criteria of prevention, inhibition and control of trace pollutants. Previous results show how low emission values of both total particles and metallic aerosol (mass basis) are compatible with occasional and unexplained outliers of PCDD/Fs (dioxins and furans) emissions. Poor or incomplete combustion, the presence of chlorine or hydrogen chloride in the gas phase, the presence of some metals -in particular Cu involved both in the formation of highly effective chlorination species- and the provision of active surfaces on fine particles have been identified as the main factors leading to PCDD/Fs formation and release (Lee, 2008). An efficient continuous monitoring of the plant performance, penetration of the submicron aerosol through the filtration system and the fine fraction copper content (≈ 0,8µm) are needed to control both these emissions and PCDD/Fs occasional emissions.

1. Introduction

Trace emissions of both heavy metals (HM) and PCDD/PCDFs from MSWI are subjected to tighten regulations (Directive 94/67/EC). MSWI results on trace heavy metals and PCDD/Fs emission as a consequence of both the contribution of sludge minor or trace components and the formation of many organic products of incomplete combustion. The prevention, minimization and control of such emissions require a deep understanding on the mechanisms of gas-solid partitioning as well as on the aerosol dynamics even along the earlier processing steps. Transition metal species, such as Cu and in a lesser extent Fe compounds, have been identified as very efficient catalysts. Nowadays neither BAT "best available technologies" nor end-of-pipe approach ensure an stable of HM and/or PCDD/Fs emission; thus, the starting hypothesis of this work is stated as "to prevent the PCDD/Fs emission through the early separation of chemically active metals as well as to minimize HM emissions preferentially concentrated in the most penetrating size range -<1µm-" (Peña et al., 2009a and 2009b).

Results from a 1-year intensive monitoring campaign on a MSWI located within a densely populated area of about one million inhabitants (Biscay) are presented. All major process streams were sampled to quantify heavy metal loadings (raw sludge, bottom ash, fly ash, stack gas). The seasonal feed variability was taken into account: 120-170t sludge/day, 999-2885m^3 fuel-gas/day, 12-29t bottom-ash/day, humidity, physical state and chemical composition (ICP-MS and SEM-EDS); moreover, the aerosol evolution seggregated by particle size along the line was characterized to study which the influence of each process stage has on the aerosol concentration and composition. The core of PM control is an electrostatic precipitator (ESP) -100 kV of nominal voltage at >200ºC-. Directly downstream of the ESP a double wet scrubber system separates, mainly, the VOCs and condensates. Figure 1 shows the incineration/depuration process line and the sampling points of fly ash along the line

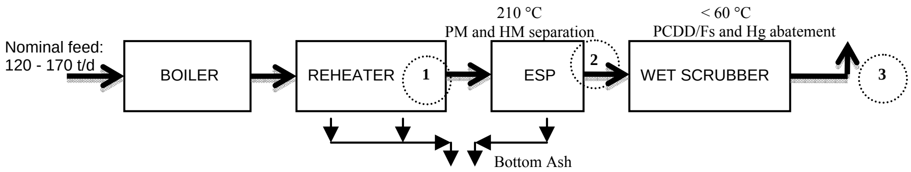
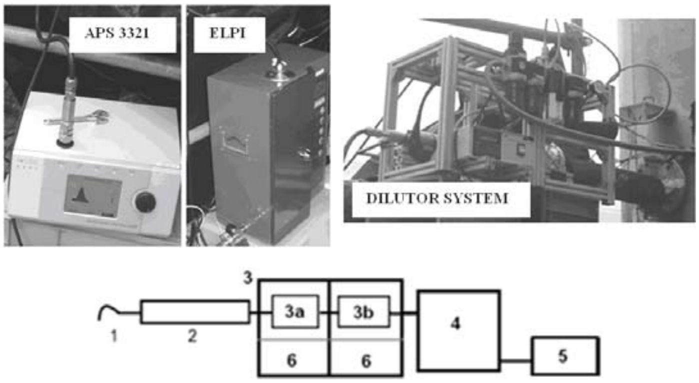


Figure 1: Off-gas processing flow diagram. Bottom ash and fly ash sampling points (1.-Upstream of the ESP; 2.-Downstream of the ESP; 3.-Stack).

Electrostatic precipitator theory defines the penetration window within the size range of trace metals occurrence (between 0,4 and 1 µm -it depends on the particle electrical characteristics, ESP regulation, etc.-). Therefore this work aims to ascertain how the fractional efficiency could be related to metal concentration and how this efficiency can be improved through manipulation of operation variables, such as the applied voltage.

2. Methodology

Since both real-time monitoring parameters and specific characteristics of metallic aerosol are needed, a complex experimental campaign was designed combining the techniques suitable for both time scales (Ferge, 2004), (Lind, 2003). The characterization method is based on a combined methodology includes size-seggregated real-time monitoring of aerosol and size-seggregated time-integrated measurement of particle matter for samples characterization (cascade impactor stages) were gathered upstream and downstream of the electrostatic precipitator for further analyzed (ICP-MS for elemental analysis and SEM-EDS). Temporal evolution of total number concentration of fine particles as well as the particle size distributions was obtained using real time aerosol analyzers -Electrical low pressure impactor "ELPI" (up to 10 µm of d_{ae}) and fly of time spectrometer "Aerosol particle sizer - APS 3321" (up to 20 µm of d_{ae}) under different process conditions (stable operating conditions means that both the main variables of the process and the ESP regulation are under nominal and constant values; on the other hand, variable operating conditions means the regulation of the line and/or of the ESP are unstable)-; figure 2 shows the set-up of the real time analyzers with the dilution systems to condition the flow gas sampled to the analyzers requirements. In addiction to this, a complete study of the operating conditions was carried out to search any possible relation between the evolution of the aerosol concentration and its composition with the plant performance (e.g. flow rates and composition of the process streams, applied voltage (ESP), temperatures, etc.).



(1) Nozzle	**(4) Real time analyzer**
(2) Probe	- Electrical low pressure impactor -ELPI-
(3) Dilution system	- Time of fly spectrometer -APS 3321-
(3a) Hot dilutor	**(5) Pump (ELPI)**
(3b) Cold dilutor	**(6) Temperature and flow controller** (air pressure)

Figure 2: Real time set-up. (Up) Aerosol analyzer and dilution system. (Down) Sampling assembly -ISO/FDIS 23210 “Stationary source emissions – Determination of PM10/PM2,5 mass concentrations in flue gas – Measurement at low concentrations by use of impactors”-.

Fractional efficiency of the 2-fields ESP and its operating conditions influence -voltage, rapping cycles, etc.- have been evaluated. Required performance was set on the major size range of occurrence for the active metals (mainly Cu, as justified below).

3. Results

Time-integrated measurements using cascade impactors show how the total concentration of aerosol decreases four orders of magnitude in mass after the electrostatic precipitator, thus the total efficiency of the ESP is very high. Aerosol particle size distribution is biased to the submicron range downstream of the electrofilter where the total concentration of particle matter is around 1 - 3 mg/Nm^3 -the accuracy of the measured particle size distributions is relative to the total mass collected from each sampling point-. Figure 3 shows the evolution of the aerosol particle size distribution along the line under different operating and regulating conditions of the process and mainly of the ESP.

Since the values for total particulate concentration at the stack and downstream of the ESP, HM control should be focused at the outlet of the ESP. In other words, wet scrubbers do not enable a significant reduction of submicron aerosol. Modeling results show that applied voltage has the greatest influence on the fractional efficiency of the ESP and thus, on the aerosol emission (Legarreta, et al., 2010). The most significant difference between particle size distributions downstream of the ESP under different operating conditions appears around 2 microns -cut diameter of the cascade impactors-.

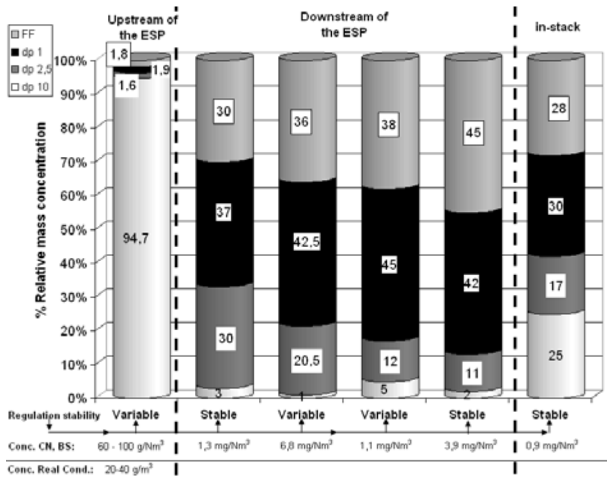


Figure 3: Particle size distribution along the line depending on the applied voltage(ESP)

Real time measurements show, considering an uniform density of 1 g/cm^3, the same deviation of the particle size distribution than the time-integrated measurements (<1 µm). Total number concentration measured upstream of the ESP using ELPI is around $1,5 \cdot 10^{+05}$ #/cm^3 -where the maximum values of the particle size distribution are at 0,8 µm and 0,3 µm- and downstream of the ESP is around $1,0 \cdot 10^{+04}$ #/cm^3 -where the maximum values of the particle size distribution are at 0,8 µm and below of 0,1 µm- (under stable operating conditions). Total number concentration measured upstream of the ESP using APS 3321 is around $3,0 \cdot 10^{+05}$ #/cm^3 -where the maximum value of the particle size distribution is at 2 µm- and downstream of the ESP is smaller than $2.0 \cdot 10^{+03}$ #/cm^3 -where the maximum value of the particle size distribution is at 0,8 µm- (under stable operating conditions) (Legarreta et al., 2010).

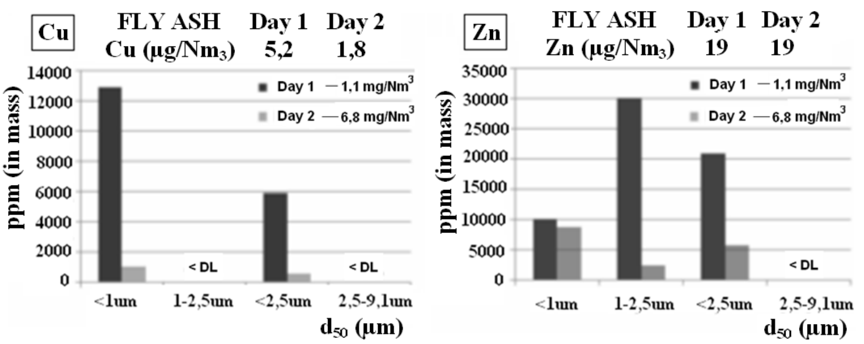
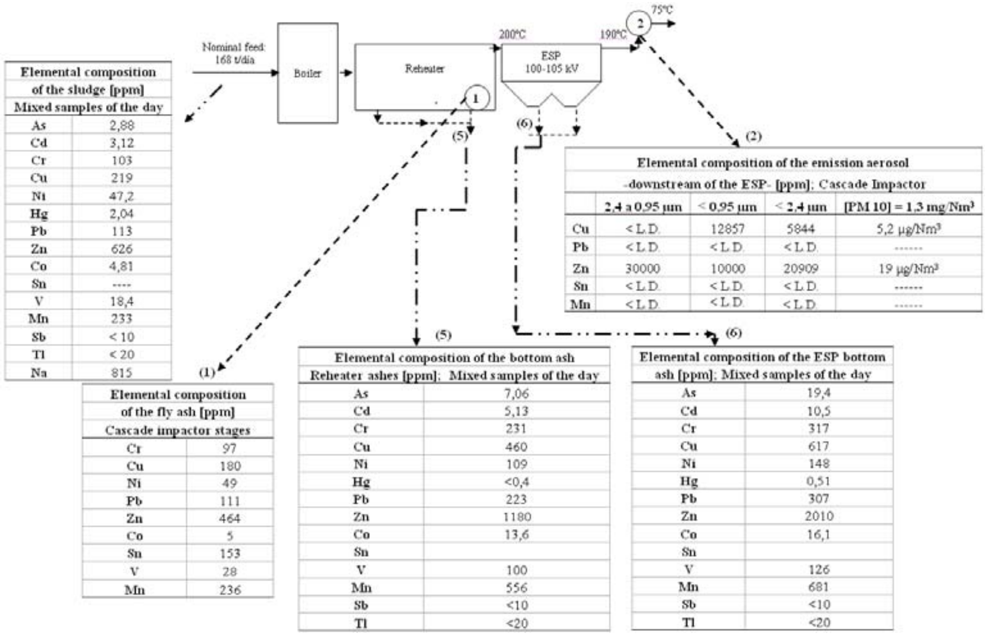


Figure 4: Cu and Zn concentrations seggregated by particle size downstream of the ESP

Copper concentration is around 13000 ppm$_w$ when total PM10 falls within its lower range (1mg/Nm^3) and falls to 1200ppm$_w$ for higher ranges (7mg/Nm^3). SEM-EDS results verify the critical size bin of occurrence for the target metals. In summary, zinc is present in the micron range whereas copper concentrates in the submicron range of the penetrating aerosol. Figure 4 shows the different behavior of the trace metals under different operating conditions and under different total concentration of aerosol.



Elemental composition of the sludge [ppm] Mixed samples of the day	
As	2,88
Cd	3,12
Cr	103
Cu	219
Ni	47,2
Hg	2,04
Pb	113
Zn	626
Co	4,81
Sn	----
V	18,4
Mn	233
Sb	< 10
Tl	< 20
Na	815

(1)

Elemental composition of the fly ash [ppm] Cascade impactor stages	
Cr	97
Cu	180
Ni	49
Pb	111
Zn	464
Co	5
Sn	153
V	28
Mn	236

(2)

Elemental composition of the emission aerosol -downstream of the ESP- [ppm]; Cascade Impactor				
	2,4 a 0,95 µm	< 0,95 µm	< 2,4 µm	[PM 10] = 1,3 mg/Nm³
Cu	< L.D.	12857	5844	5,2 µg/Nm³
Pb	< L.D.	< L.D.	< L.D.	------
Zn	30000	10000	20909	19 µg/Nm³
Sn	< L.D.	< L.D.	< L.D.	------
Mn	< L.D.	< L.D.	< L.D.	------

(5)

Elemental composition of the bottom ash Reheater ashes [ppm]; Mixed samples of the day	
As	7,06
Cd	5,13
Cr	231
Cu	460
Ni	109
Hg	<0,4
Pb	223
Zn	1180
Co	13,6
Sn	
V	100
Mn	556
Sb	<10
Tl	<20

(6)

Elemental composition of the ESP bottom ash [ppm]; Mixed samples of the day	
As	19,4
Cd	10,5
Cr	317
Cu	617
Ni	148
Hg	0,51
Pb	307
Zn	2010
Co	16,1
Sn	
V	126
Mn	681
Sb	<10
Tl	<20

Figure 5: Heavy metal concentrations along the line: 1 fly ash upstream of the ESP; 2 fly ash downstream of the ESP; 5 Reheater bottom ash; 6 ESP Bottom ash.

Morphology of the coarse fraction consists of soft agglomerates and individual particles. On the other hand, the fine fraction shows different internal and external mixed of components. Results of the SEM/EDS confirm the elemental analyses were carried out by ICP-MS. Figure 6 shows some typical examples of the particle morphologies seggregated by particle size -Electrical low pressure impactor stages-:

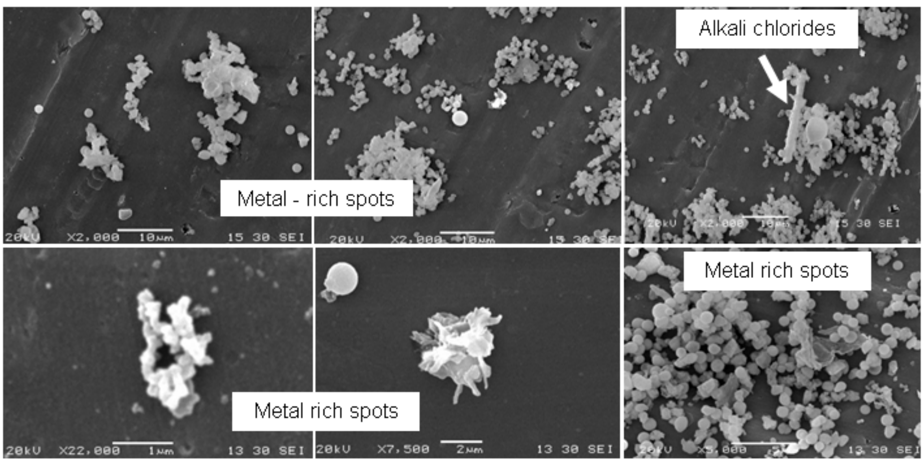


Figure 6. General morphology of fly ash. (Up) Coarse fraction. (Down) Fine fraction

4. Conclusions

Technical feasibility for time-integrated (cascade impactors) and real-time (ELPI and APS 3321) characterization of size-seggregated aerosol upstream and downstream of an ESP has been substantiated during the experimental campaign in a MSWI line.

Although the incineration line emissions of both total particles and metallic aerosol are low, there are some occasional episodes of high emissions of PCDD/Fs which are not explained with a simple correlation of the quality of the sludge or with the operating conditions. Real-time size distribution monitoring -up to 3 micron- directly upstream and downstream of the electrostatic precipitator (hot-side) allows for an effective operation control of the aerosol emissions.

Cu and Zn are found in the submicron range composition of the fly ashes (and in emissions). Copper content of the particles penetrating the ESP has been identified as the most promising way to control the dioxin-furans emission because other catalysts (Fe, Zn) enter into the wet scrubbing at a constant rate. Retrofitting the electrostatic precipitator has been discarded because of electrical hazards at voltages higher than 100 kV. Thus, a new membrane bag filter upstream of the wet scrubbing must be installed with the specific requirement of a 0.5% (mass basis) increase in collection efficiency at 0,8 μm. A new campaign is necessary to verify the performance of the new hybrid filtration system in this particle size range getting a greater amount of mass to get more representative samples for further analysis (e.g. ICP-MS).

5. References

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