



## Trace metals removal through a catalytic hybrid filter during cofiring of different biomass waste materials



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### HIGHLIGHTS

- Trace elements (TEs) removal through a Catalytic Hybrid Filter System was evaluated.
- In the tests, olive tree pruning was cofired with refuse derived fuel and compost.
- TEs capture was strongly affected by size particle and the Ca content in ashes.
- Hg enrichment was enhanced with the unburned carbon content in fly ashes.
- Cd, Sb and Pb retention increased with sulphur concentration in ashes.

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### ABSTRACT

This paper aims at evaluating trace elements (TEs) removal during biomass cofiring in a fluidised bed pilot plant (1 MWth) equipped with a Catalytic Hybrid Filter System (CHFS), as air pollution control device, which combines electrostatic precipitation (ESP) and fabric filter (FF) in a unique approach to develop a compact but highly efficient system. One biomass (olive tree pruning (OP)) and two different waste materials (municipal refuse derived fuel (RDF) and compost (CO)) were employed in the cofiring tests, to evaluate the impact of the fuel in the process.

TEs control through the CHFS as well as the effect of this system on mercury speciation, were evaluated. In addition, different factors which may be involved in TEs retention, such as ash matter composition and fly ash particle size, were investigated.

Significant removal efficiency was achieved at the CHFS for most TEs studied, even for the most highly volatile TEs such as Hg and Se (40–60%), Cd (50–70%) and Sb (80–90%). Similar trends for TEs capture were observed for both fuel mixtures, obtaining the highest removal rates for Cu, Pb, Cr and Zn. However the retention of most TEs was significantly affected by the fuel employed, as consequence of the different composition and characteristics of ashes generated in each process.

The capture of most TEs was seen to be highly influenced by the calcium content in fly ashes, while TEs of higher volatility were seen to be preferably retained in the finest size particles (<53 μm) from the catalytic FF module, despite of the fuel used, and this enrichment was enhanced with the unburned carbon content, in Hg case, and with sulphur and concentration, for Cd, Sb and Pb.

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## 1. Introduction

Trace elements (TEs) emission is one of the major environmental concerns for coal combustion as it constitutes a global air pollution problem, attracting more interest and received increasing regulatory attention in recent years.

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The cofiring of biomass with coal is becoming popular in the last years, as biomass is considered carbon-neutral [1]. In contrast to biomass fuels, alternative fuels such as wastes, employed as the secondary fuels in co-combustion, can become highly problematic with respect to emissions, in spite of their low cost, containing significantly higher TEs contents than coal.

The behaviour of trace elements during fuel combustion is known to be influenced both by the fuel properties and combustion conditions [2]. During combustion, TEs in the fuels usually undergo complicated chemical and physical transformations, being

## Nomenclature

BA	bottom ash	ICP-MS	inductively coupled plasma mass spectrometry
BFBC	bubbling fluidized bed combustion	LOI	loss of ignition
CHFS	Catalytic Hybrid Filter System	NTP	standard or Normal conditions of temperature and pressure ( $T = 273 \text{ K}$ , $P = 760 \text{ mm of mercury}$ )
CO	compost	OHM	Ontario Hydro Method
ESP	electrostatic precipitator	OP	olive tree pruning
FBC	fluidized bed combustor	PM	particulate matter
FF	fabric filter	PM2.5	fine particles of diameters below $2.5 \mu\text{m}$
FTIR	Fourier transform infrared spectroscopy	PTFE	polytetrafluoroethylene
GFAAS	graphite furnace atomic absorption spectrometry	$Q_{i,in}$	incoming stream
$\text{Hg}^{2+}$	oxidized mercury	$Q_{i,out}$	outcoming stream
$\text{Hg}^0$	elemental mercury	RDF	refuse derived fuel
$\text{Hg}^t$	total mercury	RE	relative enrichment
HGAAS	hydride generation atomic absorption spectrometric	TEs	trace elements
ICP_AES	inductively coupled plasma atomic emission spectroscopy	USEPA	environmental protection agency from USA

released and redistributed in the bottom ash, the fly ash, and the gaseous phase [3]. TEs are mainly found in the particulate phase at the particle removal device operating temperatures. Nevertheless, many of them are volatile during combustion being enriched in the fine particle fraction which penetrates easily through the particle removal devices [4].

Control of TEs emissions from coal-fired combustion plants, is currently achieved through existing controls systems employed to remove particulate matter (PM), sulphur dioxide ( $\text{SO}_2$ ), and nitrogen oxides ( $\text{NO}_x$ ). PM is commonly controlled by fabric filters (FFs) or electrostatic precipitators (ESPs). There has been extensive testing of total mercury ( $\text{Hg}^t$ ) capture through these systems on a wide range of coal-fired power plants. Plants that employ only PM controls experienced average  $\text{Hg}^t$  emission reductions ranging from 0% to 90%. Units with FFs obtained the highest average levels of control [5]. Results are influenced by a variety of factors, although the type of coal has been seen to affect strongly the mercury control, increasing mercury removal as coal rank increased [6–10].

Additional TEs control can be achieved by *sorbent injection* before the flue gas treatment system. Another approach for TEs capture is *multipollutant control*, in which TEs capture is enhanced in existing/new control devices. Research has indicated that the most cost-effective strategy for TEs control, seems to be focused on integrated multipollutant ( $\text{SO}_2$ ,  $\text{NO}_x$ , PM, and TEs) control technologies [10].

Current particulate-control systems are highly efficient for collection of trace elements associated with larger particles [11]. The most common particulate control device employed on coal-fired boilers is the ESP. Air quality standard are mainly focused on controlling fine particles ( $\text{PM}_{2.5}$ ). Since ESP collection efficiency is much lower for finer particles, hybrid filters have become a good solution because it is a superior technology that can achieve much better fine-particle collection efficiency at a lower cost than other current approaches. A hybrid filter is an air pollution control device which integrates electrostatic precipitation and fabric filter technologies to provide a compact, cost effective system with fewer and more reliable components that produce superior filtration results. The result is a system that offers the reliability of an ESP with the performance of a fabric filter. Filtration and electrostatics are employed in the same housing, providing major synergism between the two collection methods. Particles in the ESP zone will become charged and migrate towards the earthed (grounded) plate. Pre-charging of the particles before they reach the bag will enhance particle collection [12]. In addition, the dust cake formed from charged particles will be more porous, producing a lower pressure drop. The system provides ultrahigh collection efficiency overcoming, not

only the problem of excessive fine-particle emissions with conventional ESPs, but also the problem of reentrainment and recollection of dust in conventional baghouses. Moreover other important advantage is that this technology is easily adapted for new installations as well as retrofits of existing ESPs [13,14].

On the other hand, hybrid filters also have been reported to have unique advantages for mercury control over baghouses or ESPs as an excellent gas–solid contactor. Values for the capture efficiency of different TEs in hybrid filter systems with and without sorbent injection, have been reported by different authors [15,16], however most studies with respect to TEs capture by hybrid filter systems are focused on coal combustion, while little information has been reported for TEs behaviour through these systems when waste materials are used as fuel, neither pure nor cofired with biomass.

The use of waste materials normally enhances the emissions of harmful air pollutants. In addition, refuse-derived fuels (RDFs) contain elevated chlorine content in comparison with biomass, promoting an increase in the volatility of certain TEs, which could reduce the efficiency of these control devices. On the other hand RDFs present high ash content in comparison with agrosidues, favouring the interactions between TEs and the mineral matter in the combustion system, mainly in the bed region during wood and RDF cofiring [17]. At temperatures where particulate removal occurs, most TEs tend to condense on fly ash particles, achieving significant removal through an ESP or a FF [18]. However certain TEs (As, Se, Pb, Cu) were seen to be enriched in submicron particles during coal–biomass cofiring processes. In this case, the effectiveness of the ESP will be highly influenced by the fuel characteristics and the fly ash composition [17,18].

In this sense, the objective of this study was to evaluate the effect of a Catalytic Hybrid Filter System (CHFS) on trace metals behaviour and removal, during cofiring of biomass with different waste materials in a pilot-scale bubbling fluidized bed combustor (FBC). The scope of the work includes TEs control screening tests through the CHFS and the effect of this system on mercury speciation. In addition, different factors which may be involved in TEs retention, such as ash matter composition and fly ash particle size, are investigated.

## 2. Experimental

### 2.1. Utility boiler

A 1 MWth bubbling fluidised bed combustion (BFBC) plant was employed for the experiments. A scheme of the plant is shown in

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