



The fate of mercury in fluidized beds under oxy-fuel combustion conditions



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HIGHLIGHTS

- Mercury speciation in an oxy-fuel fluidized bed combustor has been analyzed.
- Sulfated Ca-based sorbent enhances the Hg uptake as particle-bound mercury.
- The higher SO₂ concentration the lower mercury oxidation from Hg⁰ to Hg²⁺.
- NO and H₂O recycled hardly affect mercury speciation at these operating conditions.

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ABSTRACT

Among the different pollutant gases released from oxy-coal combustion, mercury is the responsible for important operational issues in the CO₂ processing unit, being able to cause material corrosion. Some studies concerning the fate of mercury during oxy-coal combustion are referred to pulverized coal (PC) boilers. However, the fate of mercury emissions in fluidized bed (FB) combustors has yet to be elucidated.

In this work, mercury emissions from a 3 kW_{th} bubbling FB combustor operating under oxy-fuel combustion conditions have been evaluated. For this purpose, two Spanish Ca-based sorbents and two Spanish coals were used. The effects of type of Ca-based sorbent, the Ca/S molar ratio, temperature and recycled gases (NO, SO₂ and H₂O) typical in oxy-fuel combustion process on the distribution of mercury species have been analyzed.

It was observed that the presence of Ca-based sorbents in the combustor favored mercury fixation as particle-bound mercury which exhibited a maximum at a temperature about 925 °C corresponding to the highest degree of limestone sulfation. SO₂ recirculation inhibited the Hg⁰ oxidation and thus the mercury fixation as particle-bound mercury decreased. However, neither NO nor steam recirculation affected mercury speciation.

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1. Introduction

Oxy-fuel combustion is one of the Carbon Capture and Storage (CCS) technological options which consists of burning the fuel with a mix of pure oxygen and recycled flue gas which is mainly composed of CO₂. Therefore, the CO₂ concentration in the flue gas may be enriched up to 95% to be subsequently transported and stored. Many of the research studies are related to oxy-fuel pulverized coal (PC) combustion. However, oxy-fuel combustion of coal in fluidized bed (FB) combustors has received relatively little attention. One of the main advantages of this technology compared to

PC is the possibility of performing the in situ SO₂ retention process via Ca-based sorbents added into the combustor.

Besides SO₂, another relevant pollutant gas from coal combustion is the mercury. Electrical power plants are estimated to account for about 25% of the global anthropogenic mercury emissions into the atmosphere [1]. In oxy-fuel combustion, the mercury emission is not an environmental problem since it is not released into the atmosphere but it may represent important operational issues concerning the material corrosion, especially in the CO₂ processing unit. There are some studies concerning the fate of mercury during oxy-coal combustion in PC combustors, indicating that the average oxidized mercury emission to stack could increase from 25% to 30% with respect to conventional combustion [2]. Gharebaghi et al. [3] made a comparison of mercury partitioning

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Table 1
Composition and properties of coals and sorbents.

	Coals		Ca-based sorbents	
	Anthracite	Lignite	Granicarb	Sierra de Arcos
<i>Composition (wt%)</i>				
Moisture	2.3	12.6	CaCO ₃	97.1
Ash	31.7	25.2	MgCO ₃	0.2
Volatiles	5.6	28.7	Na ₂ O	1.1
Fixed C	60.4	33.6	SiO ₂	<0.1
C	59.64	45.43	Al ₂ O ₃	<0.1
H	1.67	2.50	Fe ₂ O ₃	<0.1
N	0.93	0.65	Cl (mg/kg)	1116
S	1.52	5.17	Hg (mg/kg)	0.0002
Cl (mg/kg)	83	189		
Hg (mg/kg)	0.27	0.11	<i>Porosity (%)</i>	
LHV (kJ/kg)	21,807	16,252	Raw	3.7
			Calcined ^a	49.0
				9.5
				51.7

^a Calcined in N₂ atmosphere at 900 °C for 10 min.

between air and oxy-fuel conditions from the predictions obtained using a combined homogeneous–heterogeneous model for PC boilers. In this study, they found that there was hardly variation in gas-phase mercury for both cases, but a significant increase in Hg_p was detected at oxy-fuel combustion conditions.

However, power plant configuration has an important effect on mercury emissions and speciation and case-by-case power plant should be studied [4]. In this context, the fate of mercury emissions from oxy-coal combustion in FBs is almost unexplored [5].

Mercury in the flue gas can be present as: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particle-bound mercury (Hg_p). When coal is burnt, mercury present in the coal vaporizes to form gaseous Hg⁰. Cooling of the combustion gases and interactions of Hg⁰ with other combustion products may result in the speciation of mercury. The partition of mercury into Hg⁰, Hg²⁺ and Hg_p depends on the flue gas composition, the amount and properties of fly ash and the flue gas quench rate [6]. When flue gases cool downstream of the combustion environment under around 600 °C, mercury can react through homogeneous or heterogeneous mechanisms to be converted into oxidized mercury or particle bound mercury [7]. The speciation of mercury depends greatly on the presence of other species like HCl, Cl₂ or SO₂. Mercury chlorination, the reaction of elemental mercury with hydrochloric acid or chloride to form mercury chloride, is considered to be dominant mercury transformation mechanism in flue gas.

In previous works performed by Gale et al. [8] for PC boilers under air conditions, it was found the presence of Ca enhances the amount of chlorinated mercury on the surface of the fly ash and in absence of Ca, Hg⁰ adsorbs onto chlorinated sites and desorbs as oxidized mercury, resulting in minimal Hg_p.

On the other hand, Fernandez-Miranda et al. [9] found that the proportion of Hg⁰/Hg²⁺ was similar when in the simulated flue gas there was not particulate matter presence and the concentration of SO₂, NO, NO₂, HCl, and H₂O was also similar, regardless of whether CO₂ (oxy-fuel combustion) or N₂ (air combustion) were the main components of the gas. Moreover, Preciado et al. [10] have been recently stated that homogeneous mercury oxidation by chlorine under oxy-firing conditions is more effective than under air-firing conditions.

Since the control of mercury emissions from coal power plants relies on an understanding of the chemistry of mercury and its interactions with various elements in the combustion system, a new factor with respect to PC, i.e., the introduction of sorbents, can influence the mercury speciation.

In this work, mercury emissions from a 3 kW_{th} bubbling fluidized bed (BFB) combustor operating under oxy-fuel combustion conditions have been evaluated. The effect of the presence of

Ca-based sorbent in the combustor, temperature, and recycled gases (NO, SO₂ and H₂O) on mercury speciation has been determined using different coals and Ca-based sorbents.

2. Experimental section

2.1. Materials

The fuels used for the combustion process were two Spanish coals, one anthracite from León and one lignite from Teruel, with a particle size of 0.2–1.2 mm. The Ca-based sorbents used were a Spanish limestone, Granicarb, and a Spanish dolomite, Sierra de Arcos, both with a particle size ranging from 0.3 to 0.5 mm. In addition, inert silica sand (0.2–0.6 mm) was fed into the combustor together with the coal and the Ca-based sorbent during the tests. Table 1 shows the composition and main properties of the materials used.

2.2. Experimental installation

The experimental installation consists of a fluidized bed reactor, and different auxiliary systems for gas supply (O₂, CO₂, H₂O, NO and SO₂), solid feeding (coal, limestone and sand as inert solid), and gas analysis. Fig. 1 shows a schematic diagram of the installation. The BFB combustor and the experimental method are described elsewhere [11].

Elemental Hg (Hg⁰) was monitored on-line by a cold vapor atomic absorption spectroscopy (CVAAS, VM3000) apparatus from Mercury Instruments. Since SO₂ is a spectral interferant, CVAAS signal was previously tested at different SO₂ concentrations in order to subtract its contribution to real Hg⁰ measurement [12,13]. Oxidized mercury (Hg²⁺) was recovered in impingers with KCl dissolution 1 M according to Ontario Hydro Method (OHM). In some experiments the complete train of impingers according to OHM was used in order to confirm the continuous Hg⁰ measurement. Mercury contents in solids (Hg_p) elutriated from the combustor (recovered in a cyclone) as well as in the bed (recovered in a drainage deposit) were determined for each operating condition. Mercury contents were directly analyzed on solids and impingers solutions using an automatized mercury analyzer LECO AMA254 gold amalgam atomic absorption spectrometer.

3. Results and discussion

Coal combustion experiments with Ca-based sorbent addition were carried out in a BFB combustor working in oxy-fuel

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