

**Mercury emissions from coal combustion in fluidized beds  
under oxy-fuel and air conditions: influence of coal  
characteristics and O<sub>2</sub> concentration**

M.T. Izquierdo\*, M. de las Obras-Loscertales, L.F. de Diego, F. García-Labiano,  
T. Mendiara, A. Abad, P. Gayán, J. Adánez

Instituto de Carboquímica, ICB-CSIC. c/Miguel Luesma Castán, 4. 50018  
Zaragoza, Spain.

\*Corresponding author: [mizq@icb.csic.es](mailto:mizq@icb.csic.es)

## **Abstract**

In this work, the fate of mercury in a bubbling fluidized bed combustor working under oxy-combustion conditions has been studied and compared with air combustion. The influence of burning three different rank coals, with sulphur content ranging from 0.65 % to 5.17 %, on Hg partitioning has been studied. The presence of limestone as sorbent for SO<sub>2</sub> capture as well as the concentration of O<sub>2</sub> at the entrance of the combustor were also evaluated. Coal rank does not have a direct influence on coal partitioning. However, sulphur content of the coal is an important parameter to describe not only the high percentage of particle-bound mercury, up to 87 %, in presence of limestone but also the prevalence of Hg(0) as the main species in the gas phase when burning the lignite. The O<sub>2</sub>/CO<sub>2</sub> ratio has little effect on Hg partitioning in experiments carried out in presence of limestone at 925 °C (the optimum temperature for sorbent sulphating under oxy-combustion conditions) and little differences are found with air combustion at 850 °C (the optimum temperature for sorbent sulphating under air combustion conditions). Percentage of particle-bound mercury shows a maximum at 925 °C independently of the coal studied, which it is related with the maximum sulphur retention for each coal at this temperature.

Keywords: mercury emissions; oxycoal combustion; fluidized bed; limestone.

## 1. INTRODUCTION

The basic principle of oxy-combustion is to burn a fuel in a mixture of oxygen and recycled flue gas (RFG) instead of air [1-3]. So, flue gas is mainly composed by CO<sub>2</sub> and H<sub>2</sub>O, and the CO<sub>2</sub> rich gas is purified and then cooled, compressed and ready to transport and storage.

In addition to the advantage to avoid the CO<sub>2</sub> separation from flue gas, NO<sub>x</sub> emission can be reduced to less than one-third of that of combustion in air because not only of the reduction of thermal NO<sub>x</sub> (due to the air-nitrogen elimination) but also because of the reburning of recycled NO<sub>x</sub> with volatiles as well as reaction of recycled NO<sub>x</sub> with char [1, 3, 4]. On the other hand, the SO<sub>2</sub> concentration increases during oxycoal combustion with RFG [1, 5] and gas purification by flue gas desulphurisation systems is mandatory because of the high risk of in-furnace corrosion and CO<sub>2</sub> transportation systems [6].

Fluidised bed (FB) combustors working under oxyfuel conditions allow the *in situ* flue gas desulphurisation by the injection of the appropriate sorbents in the boiler [7]. With respect to the accepted advantages of the circulating fluidised bed (CFB) [8, 9], the abatement of SO<sub>2</sub> is also an important issue in oxycoal combustion.

Among trace elements coming from coal combustion, mercury is a leading concern among the air toxic metals because of its volatility, persistence, bioaccumulation in the environment and its neurological health impacts [10].

Mercury present in the flue gas can be found as elemental mercury, Hg(0), oxidised mercury, Hg(II), and particle-bound mercury, Hg(p). In general, mercury speciation depends on: coal properties, combustion conditions, the flue gas composition, fly ash properties, the time/temperature profile between the

boiler and air pollution control devices, and the flue gas cleaning methods, if any, in use. Mercury can be oxidized in the SCR units, which can favour its adsorption on particulate matter and removed from the flue gas in the particulate matter control devices or, because of its solubility, Hg(II) can be retained in the WFGD systems. Thus, mainly Hg(0) would be released [11].

There are some studies concerning the fate of mercury during pulverized coal (PC) oxy-combustion indicating that the average oxidized mercury emission to stack are higher regarding conventional combustion [12, 13]. Recent studies during air and oxy-fuel firing transitions at the Callide Oxy-fuel Project [14] have shown that oxy-fuel fly ash contains lower amounts of mercury than air fired fly ash; the authors found this trend consistent with the lower LOI values.

For FB boilers, two new aspects have to be added regarding PC oxy-combustion: the presence of a sorbent, which it is expected to have some mercury capture ability, and the type of reactor, which allows extended contact time between the sorbent and the Hg.

The effect of combustion temperature and recycled gases (NO, SO<sub>2</sub> and H<sub>2</sub>O) on the fate of mercury emissions from coal combustion in fluidized beds (FB) has been previously studied [15]. In that study, it was concluded that the particle-bound mercury exhibited a maximum at a temperature about 925 °C, with different Ca-sorbents and Ca/S ratios which coincided with the highest degree of the limestone sulphation and so the lowest SO<sub>2</sub> concentration.

However, the fate of mercury comparing air and oxy-combustion mode in FB, under different O<sub>2</sub> concentration at the entrance of the combustor and with different rank coals exhibiting different sulphur content is almost unexplored.

The quality of CO<sub>2</sub> to be transported and sequestered has been subject of research, concerning impurities participating in mineralization and precipitation reactions in sequestration conditions [16]. However, the role of mercury during CO<sub>2</sub> transport has not been deeply studied, in particular corrosion issues on steel pipelines when some humidity is present [17].

Moreover, for coal oxy-combustion, mercury is not an environmental issue alone but also an operational issue, particularly about where mercury could accumulate within the CO<sub>2</sub> processing unit. The removal of Hg is necessary to prevent Hg attack on the aluminium heat exchangers [18, 19].

In this work, mercury emissions from a bubbling fluidized bed (BFB) combustor burning three different rank coals with a wide range of sulphur content operating under oxy-fuel conditions have been evaluated, testing the influence of oxygen concentration at the entrance of the combustor, comparing with air combustion baseline and the presence or absence of limestone in the bed.

## **2. EXPERIMENTAL**

The experimental facility used was a BFB combustor of 3 kW<sub>th</sub>. It consists of a fluidized bed combustor and different auxiliary systems for gas and solid supply, solid recovering and gas analysis. Temperature, pressure and gas flow were followed on-line. More details of the experimental installation can be found elsewhere [20].

CO<sub>2</sub>, CO and SO<sub>2</sub> concentrations at the exit of the combustor were continuously analysed continuously by a Non-Dispersive Infrared analyser (NDIR, Siemens/Ultramat 23) and O<sub>2</sub> concentration was continuously analysed in a paramagnetic analyser (Siemens/Oxymat 6).

Sampling of gaseous mercury, Hg(0) and Hg(II) in the gaseous outlet stream was performed at steady state operation [15, 21]. Oxidized mercury was trapped in impingers containing 100 ml of KCl 1M. Saturated KMnO<sub>4</sub> (about 5 %) solution was added to the KCl during the breakdown to remove SO<sub>2</sub> by the reaction between KMnO<sub>4</sub> and SO<sub>2</sub> preserving the mercury in sample solutions. Mercury content in impingers solutions was analysed using an automatized mercury analyzer LECO AMA254 gold amalgam atomic absorption spectrometer. Elemental Hg was monitored on-line by a cold vapor atomic absorption spectroscopy (CVAAS-VM300) apparatus. As SO<sub>2</sub> is a spectral interferant, CVAAS signal was previously tested at different SO<sub>2</sub> concentrations in order to subtract its contribution to Hg real measurement [22].

Mercury content in solids elutriated from the combustor (recovered in a cyclone, CS) as well as bed materials (recovered in a drainage deposit, BS) was determined for each operating condition as a total Hg(p). Mercury contents were directly analysed on solids using the LECO AMA254 apparatus.

In order to evaluate the quality of Hg measurements, one of the experiments was repeated twice (lignite combustion at 925 °C under ratio O<sub>2</sub>/CO<sub>2</sub> of 35/65) in two different days and the same experimental procedure was followed. In addition, two different Hg(0) measurement procedures were used during the experiment carried out with the anthracite under ratio O<sub>2</sub>/CO<sub>2</sub> of 35/65 in presence of limestone: Hg(0) gas was determined on line with the VM3000 device and, simultaneously, the complete train of impingers according to OHM was used in order to confirm the continuous Hg(0) measurement. In these cases, solid samples from bed and cyclone were also obtained and Hg content determined in AMA254 device.

Tests were conducted under air or oxy-fuel conditions with an anthracite (A) coming from León (Spain), a high volatile bituminous coal (B) coming from Cerrejón (Colombia) and a lignite (L) coming from Teruel (Spain). A Spanish limestone (Granicarb) was used for sulphur capture. Main characteristics of the materials are given in Table 1.

Table 1. Analysis of coals and limestone.

wt %	Anthracite	Bituminous	Lignite	wt %	Limestone
Proximate				CaCO <sub>3</sub>	97.1
Moisture	2.3	5.2	12.5	MgCO <sub>3</sub>	0.2
Ash	31.7	12.9	25.2	Na <sub>2</sub> O	1.1
Volatiles	5.6	32.7	28.7	SiO <sub>2</sub>	<0.1
Fixed Carbon	60.4	49.2	33.6	Al <sub>2</sub> O <sub>3</sub>	<0.1
				Fe <sub>2</sub> O <sub>3</sub>	<0.1
Elemental					
C	59.64	65.63	44.43		
H	1.67	4.64	2.50		
N	0.93	1.50	0.65		
S	1.52	0.65	5.17		
Sulphur forms					
Pyritic	1.50	n.d.	1.05		
Sulphate	0.02	n.d.	1.76		
Organic*	0.00	n.d.	2.36		
Hg, mg/kg	0.274	0.056	0.11	Hg, mg/kg	0.0002
LHV (kJ/kg)	21807	25398	16252		

\*by difference

n.d.: not determined

To ensure constant Ca/S molar ratio the coal and the limestone were fed together. Sand was fed separately. It was introduced inside the FB in order to short the residence time of the sorbent in the fluidized bed reactor and, accordingly, to ensure the sorbent reaching the steady state in each experiment. In all the experiments the total inlet gas flow was constant (2.23 Nm<sup>3</sup>/h) and the O<sub>2</sub> in the flue gas was around 4 % (d.b.). Detailed description of the experimental procedure can be found elsewhere [7, 15, 20].

### 3. RESULTS AND DISCUSSION

A summary of the experiments carried out in this study is depicted in Table 2.

Table 2. Summary of the experimental conditions and Hg mass balance (O<sub>2</sub> in flue gas around 4 %).

Coal	T °C	O <sub>2</sub> /CO <sub>2</sub> %	Ca/S	Coal g/h	Limestone g/h	SO <sub>2</sub> vppm	SR* %	Hg <sub>out</sub> /Hg <sub>in</sub> %
A	850	AIR	3	340	50	217	87.2	74.0
	925	25/75	3	397	50	361	69.5	74.2
	925	35/65	0	593	-	3047	0.0	73.6
	925	35/65	3	584	85	699	71.1	82.2
	925	45/55	3	780	100	925	74.7	84.3
B	850	35/65	3	530	30	891	24.8	76.4
	925	35/65	0	530	-	1298	0.2	81.9
	925	35/65	3	530	30	761	36.5	87.4
	950	35/65	3	530	30	1068	18.0	79.3
L	850	35/65	3	689	350	6560	68.2	96.5
	925	35/65	3	699	350	2651	77.1	118.2
	950	35/65	3	687	350	3593	48.5	95.7

\*SR: sulphur retention

Overall mass balance was obtained with the relation of total output mercury to total input mercury. Total input Hg was obtained considering coal and limestone feed rate. Total output mercury was calculated by the total gas mercury (elemental and oxidized), Hg(0) and Hg(II), and the total mercury in CS and in BS, Hg(p). Hg mass balance for the experiments (Table 2) is in the range of 73.6-118.2 % (within the range 70-130 %) and the standard deviation of these values is <6.0 %, which was implicated that the results are acceptable [23].

Repeated experiment with lignite combustion at 925 °C under ratio O<sub>2</sub>/CO<sub>2</sub> of 35/65 was carried in two different days and the difference of Hg(0) and Hg(II) concentration in the gas was lower than 7 %. In the case of Hg concentration in solids the difference was lower than 9 %.



The results of Hg(0) concentration obtained by on-line monitoring (VM3000 device and considering average during two hours of experiment at steady state conditions) or indirect measurement (OHM complete train of impingers) are in quite good accordance, with a difference lower than 5 %.

Mercury oxidation mainly depends on the concentration of different species present in the coal, such as Cl, N and S [24]. In present case, the content of Cl of the coals studied is negligible regarding the Cl content of the lime (937 mg Cl/Kg coal). A previous study of NO<sub>x</sub> recirculation in the same experimental installation [15] showed that the increase of NO concentration from 768 ppm to 945 ppm had a negligible effect on Hg partitioning. However, the study of the effect of sulphur content of coals under the same reactor conditions is almost unexplored.

### **3.1. Effect of sorbent and coal characteristics**

The influence of the presence of Ca-sorbent on mercury speciation was evaluated with experiments carried out with the anthracite and the bituminous coal, highest and lowest Hg content, respectively, at 925 °C and an O<sub>2</sub>/CO<sub>2</sub> ratio of 35/65. Mercury partitioning is depicted in Figure 1.

First important observation is that partitioning of mercury in presence of limestone takes place in such a way that major portion of mercury remains associated to the solids (BS and CS) for both coals. This is an important difference from conventional pulverized coal (PC) power plants where major part of mercury gets emitted as mercury vapours. Moreover, in PC fired oxy-combustor it has been reported the enhancement of Hg gas to Hg particles conversion because of oxidation [5]. So, in BFB oxy-combustion the presence of the lime and ash in the bed contribute to mercury fixation. However, it has

been described that fly ashes are the channel via which mercury oxidation under oxy-combustion occurs, but these hardly retain any mercury unless unburned carbon content is high [25]. In present case, combustion efficiencies were previously reported higher than 98 % [7], so the presence of unburned carbon is limited to fix mercury in the CS. Calcium content of coals has been reported as Hg oxidation promoter [26, 27]; however, the Ca content of the studied coals in the present work is negligible in front of the amount of lime added into the bed. Thus, the only explanation is the mercury fixation due to the presence of lime in the bed. The reaction of  $\text{SO}_2$  with  $\text{CaO}$  may have created active sulphur sites on the bed solids which can chemisorb  $\text{Hg}(0)$  in the gas phase to produce sulphur-bound Hg on the BFB solid surface. In addition, the presence of  $\text{CaO}$  with  $\text{SO}_2$  and  $\text{H}_2\text{O}$  cause mercury oxidation, which can be more easily adsorbed by the ashes, even with low unburned carbon contents [15, 27].

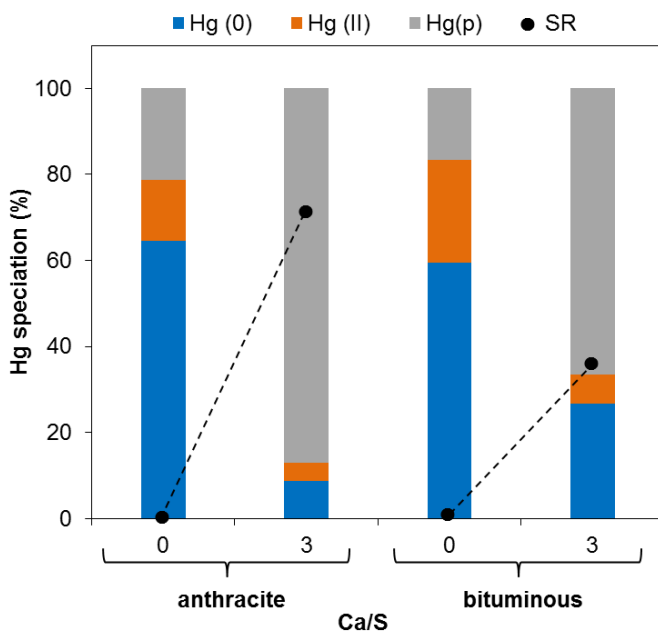


Figure 1. Effect of limestone addition on Hg partitioning in experiments carried out at 925 °C under an  $\text{O}_2/\text{CO}_2$  ratio of 35/65.

Despite partitioning of mercury takes place in such a way that major portion of mercury remains associated to the solids, in the case of bituminous coal Hg(p) represents 66.5 % facing 88.1 % in the case of anthracite. This fact could be explained in terms of lower S content of bituminous coal, which led to use a limestone feed rate near one third less than that used for the anthracite to maintain Ca/S=3; the active sites created for mercury retention might be limited under these conditions. Accordingly, Hg(0) percentage in the gas phase is significantly higher for bituminous coal. The percentage of Hg(II) is quite similar for both coals indicating that once the mercury is oxidized it is fixed directly. Regarding Hg(0) concentration, it increases from 5.3  $\mu\text{g}/\text{m}^3$  to 29.1  $\mu\text{g}/\text{m}^3$  for anthracite and from 3.1  $\mu\text{g}/\text{m}^3$  to 6.5  $\mu\text{g}/\text{m}^3$  for the bituminous coal if the sorbent is not present.

### **3.2. Oxy-combustion vs air combustion**

Figure 2 shows mercury speciation for experiments carried out with the anthracite under air conditions and under oxyfuel conditions. In this case, the temperature used for the experiments was different. It has been found that optimum temperature to reach calcining conditions and maximize sulphur retention under air combustion in FB combustors is around 850 °C [28, 29]. However, the presence of high CO<sub>2</sub> concentrations inside the bed under oxy-combustion affect the limestone behaviour and higher temperature, around 925 °C, is needed to reach calcining conditions and a maximum sorbent conversion [7]. So, in order to compare mercury emissions under air conventional and oxycoal combustion conditions, two different temperatures were used: 850 °C and 925 °C, respectively.

As can be seen in Figure 2, either under air combustion conditions or under oxycoal combustion conditions mercury is mainly retained in the solids; however a significant level of mercury are present in the flue gas, being prevalent elemental mercury species. Despite at 850 °C of temperature it is expected lower Hg vaporization rate than that corresponding at 925 °C (oxyfuel conditions), Hg(p) percentage are in the same range, indicating the prevalence of the mechanism of active sites creation due to lime addition. Low unburned carbon are expected, as the combustion efficiencies were near 100 % when working at optimum air or oxy-firing conditions; the analysis of the unburned carbon is limited because some unconverted sorbent (carbonate to oxide) could be present and the C content coming from coal, i.e. unburned carbon, could be mixed up with that C coming from the sorbent. This represents a difference from PC boilers in which fly ash with >5% LOI could have a great impact on mercury capture. It has been shown that LOI values are lower in oxy-firing indicating better burnout compared to air-firing and, accordingly the oxy-fuel fly ash contains lower amounts of mercury [14].

The increase of O<sub>2</sub> in the gas fed under oxy-combustion conditions seems to have little effect on Hg partitioning between particle-bound Hg and gas species. However, there is a slight increase of Hg(p) percentage probably favoured by the higher inventory of limestone in the bed to maintain Ca/S=3 (see Table 2). Under oxy-combustion conditions, at a O<sub>2</sub>/CO<sub>2</sub> ratio of 45/55 it can be found the highest Hg(p) percentage, which coincides with the highest SO<sub>2</sub> retention value (SR) meaning the highest formation of calcium sulphate available as active centres promoting Hg(0) chemisorption.

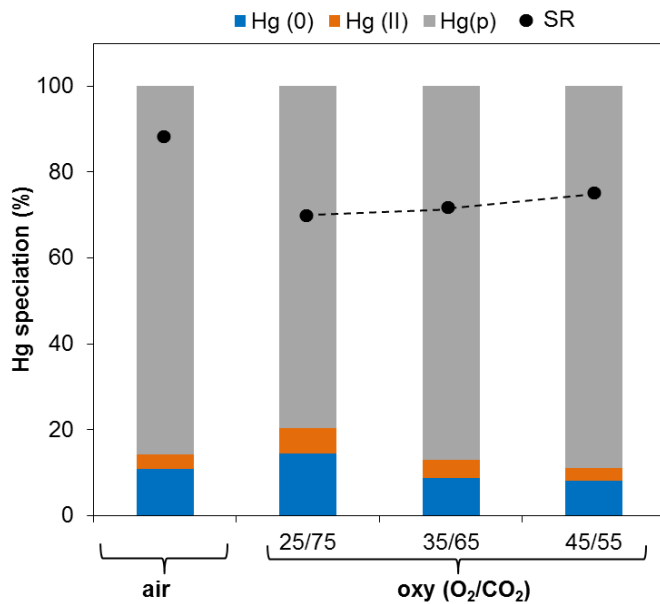


Figure 2. Effect of combustion conditions on Hg partitioning in experiments carried out with anthracite at 925 °C for oxy-combustion conditions and 850 °C for air combustion conditions and Ca/S=3 (SR: percentage of SO<sub>2</sub> retained).

This trend is not followed under air combustion conditions, where SR percentage is significantly higher than that observed for oxy-combustion conditions. It was hypothesized that the capture of Hg(0) in the presence of SO<sub>2</sub> and a Ca-based sorbent may occur through a chemisorption mechanism, while the nature of the adsorption of Hg(II) molecules may be explained through a physisorption mechanism [30]. The effect of temperature studies further supported this hypothesis. Increasing the system temperature, from 850 °C under air conditions to 925 °C under oxy-combustion conditions, caused an increase in Hg(0) uptake by the sorbent in the presence of SO<sub>2</sub>. However, the increase in temperature resulted in a significant decrease in the Hg(II) uptake in the absence or presence of SO<sub>2</sub>. The availability of Hg(0) and Hg(II) in the gas phase is also related with the role of SO<sub>2</sub> inhibiting mercury oxidation in presence of water vapour [31] through a homogeneous mechanism involving the scavenging of OH-type radicals, which is responsible of mercury oxidation in gas phase. Therefore, the SO<sub>2</sub> concentration could be an important parameter

for this mechanism as is described by Zhao et al. [32] and could explain not also the partitioning between Hg into solids and gas, but also partitioning into Hg(0) and Hg(II) in the gas phase. SO<sub>2</sub> concentration for the experiment carried out under air combustion conditions is the lowest among experiments depicted in Figure 2. This fact would mean that mercury oxidation in the gas phase is favoured and the physisorption of the oxidized mercury is favoured at 850 °C, but under these conditions Hg(0) chemisorption is not promoted at the same extent that under oxy-combustion conditions. Accordingly, Hg(0) percentage is slightly higher under later conditions.

Comparing Hg(0)/Hg(gas phase) ratio at increasing O<sub>2</sub> concentration under oxy-combustion conditions there is not clear trend, and an average value of 70±3 % is found, indicating that O<sub>2</sub> has limited Hg(0) oxidation under these conditions, as it was also found by other authors [33], despite the reducing condition induced by the O<sub>2</sub>-CO<sub>2</sub> mixture favouring the vaporization of mercury [5].

### **3.3. Effect of coal characteristics**

Figure 3 depicts the influence of type of coal on mercury partitioning under the same oxy-combustion conditions: 925 °C of temperature, O<sub>2</sub>/CO<sub>2</sub> ratio of 35/65 and Ca/S ratio of 3.

It is well known that Hg content is not a function of coal rank (i.e., one coal type does not have inherently lower Hg concentrations than another coal type). In addition, Hg concentrations in the different coals cannot be directly related to the amount of Hg emissions emitted from boilers burning these coals. Other coal properties can affect the theoretical potential level of Hg emissions that would occur in the absence of applying any Hg emissions controls. For example, coals with higher heating values require less coal to be burned to

produce a given electricity output and, thus, lower mercury emissions rate.

Other important parameter is the heteroatoms content (Cl, N, S), which lead to the homogeneous mechanism of mercury oxidation and capture on fly ash [32].

In this study, it is noteworthy that mercury and sulphur content of three coals used are quite different as well as heating values, as can be seen in Table 1.

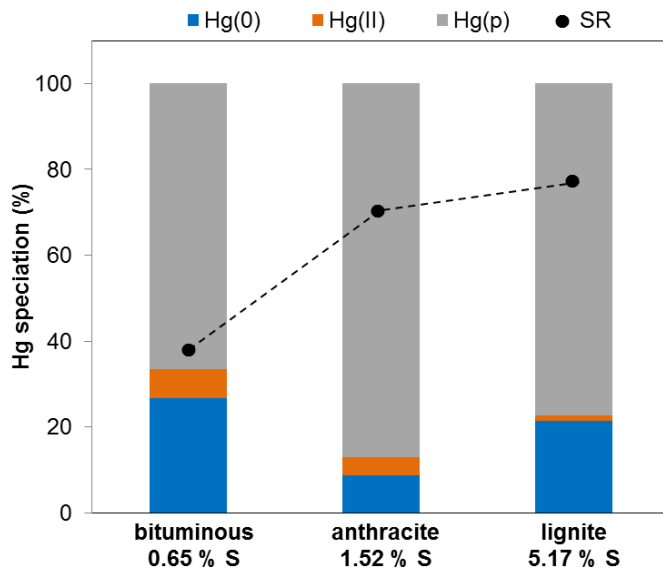


Figure 3. Hg partitioning in experiments carried out at 925 °C under an O<sub>2</sub>/CO<sub>2</sub> ratio of 35/65 and Ca/S ratio of 3.

As can be seen in Figure 3, Hg(p) is the prevalent species found during the experiments; however, anthracite exhibits the highest Hg(p) percentage despite SR values is not the highest, which corresponds to lignite. The effect of both S-sites over the Ca-sorbent and the high SO<sub>2</sub> concentration could result in a suppression of Hg fixation in the case of lignite under a mechanism described by Uddin et al. [34] using both treated and untreated commercial activated carbons (ACs): sulphur dioxide, O<sub>2</sub> and H<sub>2</sub>O were shown to be required for capture on unpromoted AC, while AC pretreated with either SO<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub> removed Hg in the absence of SO<sub>2</sub>. However, the presence of high SO<sub>2</sub> concentration and S-treated AC resulted in a suppression of Hg fixation. In the gas phase Hg(0) percentage is higher for the lignite, indicating the inhibition

effect of SO<sub>2</sub> on the Hg homogeneous oxidation mechanism; the change of SO<sub>2</sub> concentration varying from 1000 to 2000 vppm was capable of decrease the extent of Hg(0) oxidation to slightly more than 10 %, as it was found by Zhao et al. [32]. This fact was also previously observed burning a lignite in FB under SO<sub>2</sub> recirculation simulation by de las Obras-Loscertales et al. [15].

Hg(p) percentage for the bituminous coal is the lowest among the three coals studied. Sulphur content of this coal is very low and the sulphur retention value is the lowest: the amount of active sites for mercury fixation would be limited for this coal. Accordingly, the mercury found in the gas phase is the highest.

The ratio Hg(0)/Hg(gas phase) does not have a direct relationship with sulphur content of the coals studied. This behaviour could be attributed to the fact that the higher S content, the higher SR values, but the SO<sub>2</sub> concentration could be higher when SR is very low as in the case of the bituminous coal. As can be seen in Figure 4, the ratio Hg(0)/Hg(gas phase) increases with SO<sub>2</sub> concentration (normalized to unit power). In the case of lower SO<sub>2</sub> concentration for the bituminous coal and the anthracite, an increase of SO<sub>2</sub> concentration near the 8 % led to a significant increase of Hg(0)/Hg(gas phase) ratio. This increase is more significant when burning the lignite: despite the high SR, the SO<sub>2</sub> concentration is four times higher than in the case of burning the bituminous coal or the anthracite. This fact is in agreement with previous studies [31, 32] indicating the homogeneous mechanism involving the scavenging of OH-type radicals limiting the mercury oxidation in gas phase. In addition, lignite has a high content of organic-bound S and lower pyritic-type S than that of anthracite, despite the high S content difference between these two coals. Notwithstanding the major product in the combustion of all S compounds



is SO<sub>2</sub>, the combustion of organic-bound S follows a different mechanism than that of other S compounds and it has been described the inhibiting effect of SO<sub>2</sub> on hydrocarbon oxidation and, accordingly, SO<sub>2</sub> is responsible for a self-inhibition in the oxidation of organic S compounds [35]. This inhibition most likely arises from its role in the removal of free radicals. This fact could contribute to an enhancement of scavenging of radicals, as described previously, which is responsible of mercury oxidation in gas phase. In any case, the consequence of burning a high sulphur content coal is a higher Hg(0) concentration, despite high levels of sulphur retention are achieved. However, the presence of the sorbent shifts the Hg partitioning to Hg(p), as it was shown in section 3.1. As an example, Hg(0) concentration when burning the lignite increases from 5.3 µg/m<sup>3</sup> to 29.1 µg/m<sup>3</sup> if the sorbent is not present.

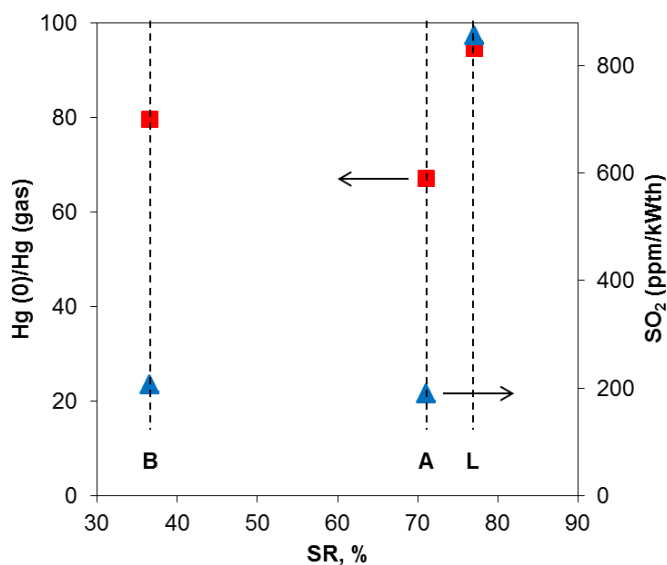


Figure 4. Influence of sulphur content of coal and SO<sub>2</sub> concentration on Hg partitioning in the gas phase (experiments carried out at 925 °C under an O<sub>2</sub>/CO<sub>2</sub> ratio of 35/65 and Ca/S ratio of 3).

### 3.4. Effect of temperature and coal characteristics

Up to this point, it has been described the impact of limestone addition on the mercury partitioning. However, those experiments were carried out at the

optimum temperature at which the highest sulphating conversion is obtained, according to previously reported results [7]. In present work, Hg partitioning was obtained for experiments carried out at different temperatures with the lignite, with the highest S content, and the bituminous coal, with the lowest S content, in order to study the correlation between sulphur reduction and mercury partitioning, as can be seen in Figure 5.

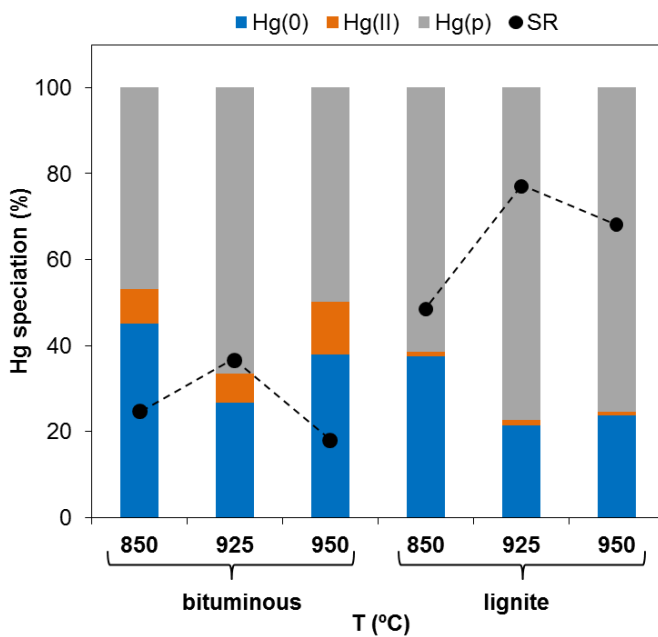


Figure 5. Hg partitioning in experiments carried out at different temperatures under an O<sub>2</sub>/CO<sub>2</sub> ratio of 35/65 and Ca/S ratio of 3.

Under high CO<sub>2</sub> concentrations, the limestone can retain sulphur in different ways depending on the temperature, according to de Diego et al. [7]; at lower temperatures sulphur retention is achieved by direct sulphating and at higher temperatures the mechanism of sulphur retention is via indirect sulphating. The high partial pressure of CO<sub>2</sub> under oxy-combustion conditions shifts the decomposition of CaCO<sub>3</sub> to higher temperatures. Therefore, at 850 °C under oxy-fuel combustion direct sulphating is the prevalent mechanism and temperature higher than 900 °C is necessary to involve indirect sulphating mechanism.

Hg(p) percentage shows a maximum at 925 °C for both coals; this fact coincides with the maximum sulphur retention (SR) for each coal as can be seen in Figure 5. Under these conditions, there are a higher amount of active sites Ca-S available for Hg(0) chemisorption. On the contrary, at 850 °C non-calcining conditions of sorbent make mercury retention on solids be lower; this fact is related with the lower SR achieved for each coal. Despite at 950 °C the sorbent is under calcining conditions, Hg(p) for the bituminous coal significantly decreases compared to the value obtained at 925 °C; this fact seems to be related to the significantly decrease of sulphur retention associated to sorbent sintering [7]. For the lignite, Hg(p) values are quite similar for both temperatures, 925 °C and 950 °C, despite the SR decreases near 10 % because of sorbent sintering at 950 °C. In this case, the high amount of limestone fed to the bed to maintain the Ca/S ratio as 3 gives enough sites for Hg fixation and Hg(p) value is maintained at that temperature.

Comparing mercury partitioning temperature by temperature for each coal, it can be seen higher Hg(p) percentage for lignite than for bituminous coal. As the sulphur content of the lignite is about eight times higher than that of bituminous coal sulphur content, the rate of limestone during the experiments carried out with lignite was ten times higher. Therefore, the availability for mercury chemisorption sites is higher when burning the lignite.

Despite the higher SR is reached for the lignite, SO<sub>2</sub> concentration is higher for this coal because the high sulphur content. This fact lead to a lower Hg(II) percentages found for the lignite at all the studied temperatures due to the inhibition of the mercury oxidation mechanism.

The results obtained in this work allow us to predict that the mercury released is mainly in the solids. However, the Hg(0) concentration in the flue gas could be important, in particular when burning high-S coals, as the lignite used in this work. High Hg(0) concentration is an important issue for coal oxy-combustion: mercury is not only an environmental issue but also an operational issue, particularly about where mercury could accumulate within the CO<sub>2</sub> processing unit; the removal of Hg is necessary to prevent Hg attack on the aluminium heat exchangers [18, 19].

For the studied coals, under the experimental conditions depicted in Figure 3, Hg(0) (considering that Hg(II) would be retained in a WFGD system) emissions were 3.1, 5.3 and 6.9 µg/Nm<sup>3</sup> (4% O<sub>2</sub> in the outlet stream) for bituminous coal, anthracite and lignite, respectively. Despite there is has not been yet established a mercury limit concentration to avoid corrosion in the CO<sub>2</sub> processing unit, it seems that it would be near that set for the gas industry of 0.01 µg/Nm<sup>3</sup> [36]. For the studied coals this limit would not be reached despite the high retention capacity on the sorbent and different mercury control systems should be used before the CO<sub>2</sub> processing unit [3, 21, 37]. However, recent studies [38, 39] showed that the removal of Hg through during compression has the potential to reduce the overall cost of oxy-fuel and represents a significant advantage that oxy-fuel has over other CCS technologies, such as post-combustion capture, which require removal of impurities prior to entering the CO<sub>2</sub> compressor unit. Thus, the oxy-combustion in circulating fluidized beds (CFBs) could capture most of the mercury; remaining mercury could be readily removed from the flue gas during compression through a gas phase, kinetically controlled, reaction with NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> [38, 39].

#### 4. CONCLUSIONS

Mercury released under oxy-combustion experiments carried out in a bubbling fluidised bed using limestone as Ca-sorbent for SO<sub>2</sub> retention is mainly in the solids. The reaction of SO<sub>2</sub> with CaO creates active sulphur sites on the bed solids which can chemisorb Hg(0) in the gas phase to produce sulphur-bound Hg on the BFB solid surface. In addition, the presence of CaO with SO<sub>2</sub> and H<sub>2</sub>O cause mercury oxidation, which can be more easily adsorbed by the Ca-S compounds, even with low unburned carbon contents, as the combustion efficiencies are higher than 98 % for all the studied coals. However, the Hg(0) concentration in the flue gas could be important, in particular when burning high-S coals, as the lignite used in this work.

It seems that there is a relationship between sulphur retention values and particle-bound mercury percentage for the coals studied under the same oxy-combustion conditions, but the effect of both S-sites over the Ca-sorbent and the high SO<sub>2</sub> concentration could result in a suppression of Hg fixation through a competitive mechanism of mercury oxidation-reduction.

The increase of O<sub>2</sub> in the gas fed under oxy-combustion conditions seems to have little effect on Hg partitioning between particle-bound Hg and gas species. The Hg(0)/Hg(gas phase) ratio at increasing O<sub>2</sub> concentration is quite similar under the studied conditions, indicating that O<sub>2</sub> has limited Hg(0) oxidation despite the reducing condition induced by the O<sub>2</sub>-CO<sub>2</sub> mixture favouring the vaporization of mercury.

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#### 6. REFERENCES

- [1] G. Scheffknecht, L. Al-Makhadmeh, U. Schnell, J. Maier, Oxy-fuel coal combustion-A review of the current state-of-the-art, *International Journal of Greenhouse Gas Control* 5 (2011) S16-S35.
- [2] T.F. Wall, Combustion processes for carbon capture, *Proceedings of the Combustion Institute* 31 (2007) 31-47.
- [3] T. Wall, R. Stanger, S. Santos, Demonstrations of coal-fired oxy-fuel technology for carbon capture and storage and issues with commercial deployment, *International Journal of Greenhouse Gas Control* 5 (2011) S5-S15.
- [4] Y. Zhuang, J.H. Pavlish, N.B. Lentz, L.L. Hamre, Mercury measurement and control in a CO<sub>2</sub>-enriched flue gas, *International Journal of Greenhouse Gas Control* 5 (2011) S136-S142.
- [5] Y. Zhuang, J.H. Pavlish, Fate of Hazardous Air Pollutants in Oxygen-Fired Coal Combustion with Different Flue Gas Recycling, *Environmental Science & Technology* 46 (2012) 4657-4665.
- [6] R. Stanger, T. Wall, Sulphur impacts during pulverised coal combustion in oxy-fuel technology for carbon capture and storage, *Progress in Energy and Combustion Science* 37 (2011) 69-88.
- [7] L.F. de Diego, A. Rufas, F. Garcia-Labiano, M. de las Obras-Loscertales, A. Abad, P. Gayan, J. Adanez, Optimum temperature for sulphur retention in fluidised beds working under oxy-fuel combustion conditions, *Fuel* 114 (2013) 106-113.
- [8] L. Jia, Y. Tan, C. Wang, E.J. Anthony, Experimental study of oxy-fuel combustion and sulfur capture in a Mini-CFBC, *Energy & Fuels* 21 (2007) 3160-3164.
- [9] K. Myohanen, T. Hyppanen, T. Pikkarainen, T. Eriksson, A. Hotta, Near Zero CO<sub>2</sub> Emissions in Coal Firing with Oxy-Fuel Circulating Fluidized Bed Boiler, *Chemical Engineering Technology* 32 (2009) 355-363.
- [10] The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport., UNEP-Chemicals, Geneva, Switzerland, 2008.
- [11] L. Sloss, Legislation, standards and methods for mercury emissions control, report no. CCC/195. IEA Clean Coal Centre, London, 2012.
- [12] A. Suriyawong, M. Gamble, M. Lee, R. Axelbaum, P. Biswas, Submicrometer particle formation and mercury speciation under O<sub>2</sub>-CO<sub>2</sub> coal combustion, *Energy & Fuels* 20 (2006) 2357-2363.

- [13] R. Spoerl, L. Belo, K. Shah, R. Stanger, R. Giniyatullin, J. Maier, T. Wall, G. Scheffknecht, Mercury Emissions and Removal by Ash in Coal-Fired Oxy-fuel Combustion, *Energy & Fuels* 28 (2014) 123-135.
- [14] R. Stanger, L. Belo, T. Ting, C. Spero, T. Wall, Mercury and SO<sub>3</sub> measurements on the fabric filter at the Callide Oxy-fuel Project during air and oxy-fuel firing transitions, *International Journal of Greenhouse Gas Control* 47 (2016) 221-232.
- [15] M. de las Obras-Loscertales, M.T. Izquierdo, A. Rufas, L.F. de Diego, F. Garcia-Labiano, A. Abad, P. Gayan, J. Adanez, The fate of mercury in fluidized beds under oxy-fuel combustion conditions, *Fuel* 167 (2016) 75-81.
- [16] E. de Visser, C. Hendriks, M. Barrio, M.J. Molnvik, G. de Koeijer, S. Liljemark, Y. Le Gallo, Dynamis CO<sub>2</sub> quality recommendations, *International Journal of Greenhouse Gas Control* 2 (2008) 478-484.
- [17] J.R. DiStefano, E.T. Manneschmidt, S.J. Pawel, Corrosion of type 316L stainless steel in a mercury thermal convection loop, Report no. ORNL/TM-13754, DOI: 10.2172/6583, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN, 1999.
- [18] H.L. Craig, Detecting mercury amalgamation of aluminium by measuring potential difference between the aluminium surface and a reference electrode, patent US5171692-A, Mobil Oil Corporation, 1992.
- [19] J.B. Bessone, The activation of aluminium by mercury ions in non-aggressive media, *Corrosion Science* 48 (2006) 4243-4256.
- [20] L.F. de Diego, M. de las Obras-Loscertales, A. Rufas, F. Garcia-Labiano, P. Gayan, A. Abad, J. Adanez, Pollutant emissions in a bubbling fluidized bed combustor working in oxy-fuel operating conditions: Effect of flue gas recirculation, *Applied Energy* 102 (2013) 860-867.
- [21] C. Gomez-Gimenez, M.T. Izquierdo, M. de las Obras-Loscertales, L.F. de Diego, F. Garcia-Labiano, J. Adanez, Mercury capture by a structured Au/C regenerable sorbent under oxycoal combustion representative and real conditions, *Fuel* 207 (2017) 821-829.
- [22] D.P. Baldwin, S.J. Bajic, D.E. Eckels, D.S. Zamzow, G.P. Miller, S. Tao, C.A. Waggoner, Testing of continuous sampling air-ICP and mercury systems as Continuous Emission Monitors at the diagnostic instrumentation and analysis laboratory. Report IS-5144. US-DOE, Ames, USA, 2001.
- [23] D.L. Laudal, M.K. Heidt, Evaluation of Flue Gas Mercury Speciation Methods, Electric Power Research Institute (EPRI), Palo Alto, CA, USA, 1997.
- [24] J. Wilcox, E. Rupp, S.C. Ying, D.-H. Lim, A.S. Negreira, A. Kirchofer, F. Feng, K. Lee, Mercury adsorption and oxidation in coal combustion and gasification processes, *International Journal of Coal Geology* 90 (2012) 4-20.
- [25] N. Fernandez-Miranda, M. Rumayor, M. Antonia Lopez-Anton, M. Diaz-Somoano, M. Rosa Martinez-Tarazona, Mercury Retention by Fly Ashes from Oxy-fuel Processes, *Energy & Fuels* 29 (2015) 2227-2233.
- [26] S. Niksa, N. Fujiwara, Predicting extents of mercury oxidation in coal-derived flue gases, *Journal of the Air & Waste Management Association* 55 (2005) 930-939.
- [27] T.K. Gale, B.W. Lani, G.R. Offen, Mechanisms governing the fate of mercury in coal-fired power systems, *Fuel Processing Technology* 89 (2008) 139-151.

- [28] J. Adanez, F.G. Labiano, J.C. Abanades, L.F. Dediego, Methods for characterization of sorbents used in fluidized-bed boilers, *Fuel* 73 (1994) 355-362.
- [29] A. Lyngfelt, B. Leckner, Sulfur capture in fluidized-bed combustors - temperature-dependence and lime conversion, *Journal of the Institute of Energy* 62 (1989) 62-72.
- [30] S.B. Ghorishi, Low concentration mercury sorption mechanisms and control by calcium-based sorbents: Application in coal-fired processes, *Journal of the Air & Waste Management Association* 48 (1998) 1191-1198.
- [31] J. Kilgroe, C.B. Sedman, R. Srivastava, C.L. Ryan, S. Thorneloe, Control of mercury emissions from coal-fired electric utility boilers: interim report., U.S. Environmental Protection Agency., Washington, D.C., USA, 2001.
- [32] Y.X. Zhao, M.D. Mann, E.S. Olson, J.H. Pavlish, G.E. Dunham, Effects of sulfur dioxide and nitric oxide on mercury oxidation and reduction under homogeneous conditions, *Journal of the Air & Waste Management Association* 56 (2006) 628-635.
- [33] H. Wu, H. Liu, Q. Wang, G. Luo, H. Yao, J. Qiu, Experimental study of homogeneous mercury oxidation under O<sub>2</sub>/CO<sub>2</sub> atmosphere, *Proceedings of the Combustion Institute* 34 (2013) 2847-2854.
- [34] M.A. Uddin, T. Yamada, R. Ochiai, E. Sasaoka, S.J. Wu, Role of SO<sub>2</sub> for elemental mercury removal from coal combustion flue gas by activated carbon, *Energy & Fuels* 22 (2008) 2284-2289.
- [35] I. Glassman, Chapter 8: Environmental Combustion Considerations, in: *Combustion* (Third edition), Academic Press, San Diego, 1996, pp. 351-433.
- [36] S. Santos, Challenges in Understanding the Fate of Mercury during Oxyfuel Combustion, MEC-7 Workshop:  
[http://www.ieaghg.org/docs/General\\_Docs/IEAGHG\\_Presentations/SSantos\\_-\\_Hg\\_Presentation\\_MEC7\\_-\\_June\\_18.pdf](http://www.ieaghg.org/docs/General_Docs/IEAGHG_Presentations/SSantos_-_Hg_Presentation_MEC7_-_June_18.pdf), Glasgow, 2010.
- [37] D. Ballester, C. Gómez-Giménez, E. García-Díez, R. Juan, B. Rubio, M.T. Izquierdo, Influence of temperature and regeneration cycles on Hg capture and efficiency by structured Au/C regenerable sorbents, *Journal of Hazardous Materials* 260 (2013) 247-254.
- [38] R. Stanger, T. Ting, L. Belo, C. Spero, T. Wall, Field measurements of NO<sub>x</sub> and mercury from oxy-fuel compression condensates at the Callide Oxyfuel Project, *International Journal of Greenhouse Gas Control* 42 (2015) 485-493.
- [39] R. Stanger, T. Ting, C. Spero, T. Wall, Oxyfuel derived CO<sub>2</sub> compression experiments with NO<sub>x</sub>, SO<sub>x</sub>, and mercury removal-Experiments involving compression of slip-streams from the Callide Oxyfuel Project (COP), *International Journal of Greenhouse Gas Control* 41 (2015) 50-59.