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Mercury release and speciation in Chemical Looping Combustion of coal

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Abstract

In the *in situ* Gasification Chemical Looping Combustion of coal (*i*G-CLC), the fuel is gasified *in situ* in the fuel reactor and gasification products are converted to CO_2 and H_2O by reaction with the oxygen carrier. This work is the first study on mercury release in Chemical Looping Combustion of coal. The fraction of the mercury in coal vaporized in the fuel reactor depended mainly on the fuel reactor temperature and the coal type. In the fuel reactor, mercury was mainly emitted as Hg^0 in the gas phase and the amount increased with the temperature. In the air reactor, mercury was mostly emitted as Hg^{2+}. In a real CLC system, mercury emissions to the atmosphere will decrease compared to conventional combustion as only mercury released in the air reactor will reach the atmosphere. However, measures should be taken to reduce Hg^0 in the CO_2 stream before the purification and compression steps in order to avoid operational problems.

Keywords: chemical looping, coal, bauxite waste, mercury, emissions

1. Introduction

Among the Carbon Capture technologies, Chemical Looping Combustion (CLC) has recently emerged as a promising option to facilitate CO_2 inherent separation at low cost [1]. The use of coal in CLC with carbon capture has been investigated as coal is regarded as increasingly important fuel in the coming years. CLC of coal can be carried out under different configurations. One of them is the *in situ* Gasification Chemical Looping Combustion (*i*G-CLC) where coal is fed directly into the fuel reactor and mixed with an oxygen carrier while steam or CO_2 are supplied as fluidizing agents (Figure 1). These gases also act as coal gasifying agents according to the following reaction scheme:

$$\text{Coal} \rightarrow \text{volatiles} + \text{char} \tag{1}$$

$$\text{Char} + H_2O \rightarrow H_2 + CO \tag{2}$$

$$\text{Char} + CO_2 \rightarrow 2\ CO \tag{3}$$

The oxygen carrier reacts with the gases produced in reactions (1)-(3) to yield CO_2 and water as products.

$$H_2, CO, \text{volatiles} + n\ M_xO_y \rightarrow CO_2 + H_2O + n\ M_xO_{y-1} \tag{4}$$

After reaction in the fuel reactor, the reduced oxygen carrier reaches the air reactor, where it is re-oxidized again with air.

$$M_xO_{y-1} + \tfrac{1}{2}\ O_2 \rightarrow M_xO_y \tag{5}$$

The selection of an adequate oxygen carrier is always a key issue in CLC, but in the case of the *i*G-CLC process, it becomes even more relevant. Ashes should be drained to avoid their accumulation in the system and some oxygen carrier can be lost together with them. Fe-based oxygen carriers are considered an attractive option due to its low cost and environmental compatibility. Besides, Fe-based materials with magnetic properties could be separated from the ashes. Thus, natural minerals [2-3] and industrial wastes [2,4] based on iron have been tested as oxygen carriers with different coals showing good performance. In our research group, it was recently reported the use of the Fe-enriched sand fraction from bauxite processing (Fe-ESF) with promising results compared to other materials [4-6].

Despite their interest, emissions of contaminants in CLC using coal have received little coverage in literature up to date and have been mainly focused on sulfur and nitrogen emissions [7-10]. However, the emission of mercury from combustion systems is a topic of growing concern due to the volatility, extremely toxic effects and tendency of mercury to bioaccumulate through the food chain. The accumulation of mercury in the human body can affect human health and generate long-lasting effects. Moreover, mercury emissions are expected to grow in the next future due to the intensive use of coal as fuel for electricity generation [11]. Mercury can be present in coal in three forms, namely clays, organic matter and sulfides (mainly pyrite, FeS_2, and cinnabar, HgS) [12]. Mercury content in coal range between 0.02-1.0 mg/kg [12], although most of the values are usually found below 0.2 mg/kg. In bituminous coals, mercury is generally associated with FeS_2 and HgS, while in sub-bituminous coals mercury is largely associated with the organic fraction [13]. These compounds decompose during combustion and mercury is liberated as Hg^0 (g). Therefore, the mode of occurrence of mercury does not affect the initial combustion transformation mechanism [14]. Nevertheless, elemental mercury Hg^0 can be either oxidized or adsorbed on other particles as flue gases cool down. The final speciation of mercury in flue gases may depend on different factors, such as concentration of Hg in the coal, the flue gas temperature and composition, the concentration and physical characteristics of the entrained ash and the time of mercury compounds in the flue gas [14]. The release of mercury in both coal gasification and combustion has been studied during last years. Following thermodynamic calculations, $Hg^0(g)$ should be the stable form in the highest temperature regions of combustors and gasifiers [15]. In the reducing conditions of a gasification flue gas, $Hg^0(g)$ will remain as the dominant form. However, when combustion flue gas cools down, $Hg^0(g)$ will react to form Hg_2^{2+} and Hg^{2+} compounds. Nevertheless, the principal oxidized form of mercury is assumed to be Hg^{2+} [14,16]. Mercury chemistry involves both homogeneous and heterogeneous reactions. Mercury chlorination has been identified as the main mercury transformation mechanism. Other possible mechanisms are related to mercury interactions with ash particle surfaces where reactive chemical species, catalysts and active sorption sites are available to convert $Hg^0(g)$ to $Hg^{2+}(g)$ and particulate mercury, Hg(p) [16]. According to this, mercury species can be classified into three main forms: $Hg^0(g)$, $Hg^{2+}(g)$ and Hg(p).

Sliger et al. [17] established that the reaction sequence for Hg oxidation is a Cl-atom recycle process. Therefore, the chlorine content in coal becomes especially important. High levels of mercury oxidation are most strongly correlated with chlorine concentrations in the coal [18]. The averaged chlorine contents in bituminous and lignite coals have been reported as 340±40 and 120±20 ppm, respectively [19]. Once a pool of Cl-atoms is established, Hg^0 is first oxidized via Cl into HgCl (eq. 6) which, in turn, is subsequently oxidized by Cl_2 into $HgCl_2$ (eq. 7) with an associated regeneration of Cl-atoms. The concentration of atomic Cl was influenced by reactions related to moist CO oxidation, chlorine species transformations and NO formation [20].

$$Hg^0 + Cl \rightarrow HgCl \qquad (6)$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl \qquad (7)$$

In addition to chlorine, O_2 and NO_2 can oxidize mercury in the flue gas. The homogeneous reaction between Hg^0 and O_2 or NO_2 was reported to be non-significant [16]. Nevertheless, these gases facilitate Hg^0 adsorption and oxidation in the presence of inorganic and carbonaceous ash particles. The heterogeneous reaction between Hg^0 and atomic oxygen to form HgO (s) on particle surfaces was proposed to explain mercury adsorption [16]. Other compounds present in gasification and combustion flue gases can also influence mercury oxidation. Moisture has been reported to be a strong inhibitor [20]. SO_2 had an inhibitory effect when high amounts of HCl are present in the flue gases [21] while NO was found to either promote or inhibit homogeneous Hg oxidation, depending on its concentration [17,20].

Focusing on the *i*G-CLC technology, the release of mercury could take place both in fuel and air reactors. The conditions of mercury release would be different in each case as the atmospheres in both reactors are quite different. In the fuel reactor, steam or CO_2 would be the major component in the gaseous atmosphere as they are used as gasifying agents. In the air reactor oxygen will be present in high concentration. The mercury found at the fuel reactor outlet will affect the quality of the CO_2 to be compressed, transported and stored which can be a concern for the CO_2 processing unit. Mercury can accumulate in the CO_2 processing unit and attack the aluminium heat exchangers. Moreover, it is known that trace quantities of heavy metals can participate in mineralization and precipitation reactions in sequestration conditions. The mercury released through the air reactor will be emitted to the atmosphere. Many efforts have been conducted during last years in order to regulate mercury emissions from coal-fired power plants. As a result, mercury-specific legislation was already set in United States, Canada and Germany. In 2012, China adopted the air pollution emission standards for coal-fired power plants, including mercury.

Therefore, the investigation of the fate of mercury in CLC systems is especially relevant. It would be interesting to know both the amounts and the speciation, Hg^0(g) and Hg^{2+}(g), in both fuel and air reactors. The present work studies for the first time the fate of mercury in coal when it is burned in an *i*G-CLC system and analyzes the differences with respect to conventional combustion. Special attention will be paid to the influence of the fuel reactor temperature on the mercury emissions during the process.

2. Materials and methods

2.1 Oxygen carrier and coal used

The Fe-enriched sand fraction (Fe-ESF) from bauxite processing in the alumina production was supplied by Alcoa Europe-Alúmina Española S.A. This bauxite waste was dried at room temperature for 72 hours and then sieved to the desired size (+100-300 μm). The dried sample was calcined at 1200°C during 18 h to ensure complete oxidation of the sample and to increase the resistance to attrition. The resulting material was used as oxygen carrier in the *i*G-CLC process and was activated before its use in the present experiments [6]. The main chemical and physical properties of the material are shown in Table 1 [8]. Anthracite from "El Bierzo" (Spain) and lignite from Teruel (Spain) were used as fuel. They were milled and sieved to the desired size (+200-300 μm). Ultimate and proximate analyses of the coals are shown in Table 2, together with the low heating value.

2.2 Experimental setup and procedure

The coal combustion experiments were performed at the ICB-CSIC-s1 unit, previously described [6]. This experimental unit was composed of two interconnected fluidized bed reactors, identified as fuel (FR) and air (AR) reactors. They were connected by a fluidized bed acting as loop seal. In this unit, coal was fed at the bottom of the fuel reactor bed, above the distributor plate and gasified by steam. The gasification products were oxidized by the oxygen carrier. Then, the reduced oxygen carrier and unconverted char particles were transferred to the air reactor. The combustion of char in the air reactor represents a decrease in the carbon capture efficiency. In order to avoid unconverted char reaching the air reactor, a carbon stripper could be placed after the fuel reactor in an industrial CLC facility [22]. In fact, the carbon stripper is one of the best options to maximize the carbon capture in an *i*G-CLC system [5]. However, the absence of a carbon stripper in this unit makes the interpretation of the effect of different operational conditions on the results obtained easier.

The oxygen carrier in the unit was 3.5 kg, around 1.2 kg in the fuel reactor. The circulation flow rate was maintained at around 4.5 kg/h and the thermal power was 550 MWth (100 g/h). Steam was used as fluidizing/gasifying agent in all the experiments and the flow to the fuel reactor corresponded to a velocity of 0.1 m/s at 900°C. In the air reactor, the air flow corresponded to a velocity of 0.5 m/s at 900°C. All the tests were performed at stoichiometric conditions, defined by a value of the oxygen-carrier to fuel ratio (ϕ) equal to unity (see eq.8). This ratio compares the oxygen supplied by the circulating oxygen carrier to the oxygen needed to burn the fuel fed. In this case, it is assumed that the state of reduction of the oxygen carrier in all cases was Fe_3O_4.

$$\phi = \frac{F_{OC} \cdot R_{OC}}{\dot{m}_{SF} \cdot \Omega_{SF}} \tag{8}$$

The temperature in the air reactor was maintained at around 950°C and the fuel reactor temperature was varied from 875°C to 930°C. A total of 18 hours of continuous operation feeding fuel and 32 hours of continuous fluidization were registered. CO, CO_2, H_2, CH_4 and SO_2 concentration in the fuel reactor outlet stream together with CO, CO_2, O_2 and SO_2 from the air reactor were recorded. Sampling of gaseous mercury (Hg^0 and Hg^{2+}) in the gaseous outlet stream of the fuel and air reactors was independently performed once steady state conditions were reached at each temperature. Then, the mercury content in the outlet stream of each reactor was measured during 30 minutes. Elemental Hg was monitored on-line by a cold vapor atomic absorption spectroscopy (CVAAS) apparatus, VM3000 from MCI. Oxidized mercury was determined according to Ontario Hydro Method. Therefore, impingers containing 1M KCl were placed in a bath at 0ºC to retain oxidized mercury. Mercury in solids elutriated from air reactor was also determined. Mercury content was directly analysed on solids and impingers solutions using an automatized mercury analyser LECO AMA254 gold amalgam atomic absorption spectrometer.

3. Results

3.1 Analysis of the anthracite combustion

The experiments with anthracite were carried out at different temperatures in the range 875-930ºC. Figure 2 shows a typical product distribution obtained once the steady state was reached in the experiment at 920ºC, both in fuel and air reactors. As it can be seen, the operation of the experimental unit was smooth and the values remained quite stable during the 30 minute measurement. CO_2 was the main product. The main unburned compounds were CO, H_2 and CH_4. It expected that the CO_2 molar flow increases with temperature while the amount of unburned compounds decreases [6]. SO_2 was detected at the outlet of the fuel reactor and reached a value close to 6600 ppm at 920ºC. At the air reactor outlet SO_2 was also detected. It was formed in the combustion of the char not gasified that reached the air reactor. Gasification is enhanced at higher temperatures in the fuel reactor and lower SO_2 emissions in the air reactor are registered [10]. At 920ºC, around 60 ppm were recorded at the air reactor outlet. Both Hg^0 and Hg^{2+} concentrations were also included in Figure 2. In the case of Hg^{2+} and according to the measurement procedure previously described, the averaged value for the whole measurement period was plotted.

The combustion performance of the Fe-ESF oxygen carrier burning anthracite can be analyzed focusing on two parameters: the carbon capture efficiency (η_{CC}) and the total oxygen demand (Ω_T). The carbon capture efficiency, η_{CC}, is the fraction of the total carbon fed converted to gas in the fuel reactor. Only CH_4, CO and CO_2 were considered, as the amount of tars and hydrocarbons heavier than CH_4 detected was negligible [6].

$$\eta_{CC} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR}]}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR}]} \tag{9}$$

The carbon capture depends on the carbon in the char formed which is already gasified, represented by the char conversion (X_{char}). All the volatiles in coal are assumed to be captured. Char conversion is calculated as the fraction of carbon in the char which is released to the FR exhaust gas stream.

$$X_{char} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} - F_{C,vol}]}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR} - F_{C,vol}]} \tag{10}$$

Figure 3 presents the values of the carbon capture (η_{CC}) and char conversion (X_{char}) for different fuel reactor temperatures in the combustion of this anthracite. In general, an increase in temperature leads to an increase in the char conversion and the carbon capture efficiency. Nevertheless, the carbon capture values reached were low, around 20% at the highest temperature tested. As it has been already observed [23], the char gasification rate of this anthracite is low and therefore, there is a significant part of the char produced in the gasification process that reaches the air reactor. This causes the carbon capture efficiency to decrease. In order to reach higher values, the use of a carbon separation unit would be advisable [22], although the analysis of its effect is not the objective of the present study. It is also relevant to note that the carbon capture and the char conversion values are very close. This is due to the low volatile content of this coal, see Table 2. Figure 3 also presents the values for the total oxygen demand (Ω_T). This parameter was calculated as the quotient between the oxygen lacking to achieve complete combustion of the gaseous compounds in the fuel reactor to CO_2 and H_2O and the oxygen demand of the coal introduced.

$$\Omega_T = \frac{0.5 \cdot F_{CO,FR} + 2 \cdot F_{CH_4,FR} + 0.5 \cdot F_{H_2,FR}}{(\dot{m}_{SF} \cdot \Omega_{SF} / M_{O_2})} \tag{11}$$

The oxygen demand decreased with increasing temperatures. In general, very low values were observed, around 1%. The oxygen demand is mainly attributed to the volatiles that escape from the fuel reactor without being converted. In the case of anthracite, the amount of volatiles is low and the Fe-ESF particles present high reactivity to the main gases in the volatiles [23,24], what would explain this low values of oxygen obtained.

3.2 Analysis of the mercury emissions

As it has been already mentioned before, the objective of this study is to analyze mercury release in the fuel and air reactors of a CLC system burning coal. The study of the mercury release using anthracite as fuel was carried out at two different temperatures, i.e. 875 and 920ºC. Figure 4 shows the scheme of the continuous rig and the streams where the mercury content was determined. First, the mercury content in the solids fed to the system was analyzed. Anthracite presented high mercury content (0.274 mg/kg coal). The mercury content in the Fe-ESF was negligible, lower than 0.0001 mg/kg. Finally, the mercury present in the fines at the outlet of the air reactor was also measured. These solids are mainly composed by coal ash. At all the temperatures analyzed, the mercury content in the fines (Hg_AR,s) was under the measure limit of the equipment (lower than 0.0001 mg/kg) and can be considered as negligible. In the gaseous outlet streams, the mercury content and the speciation (Hg^0/Hg^{2+}) at the exit of the fuel and air reactors was determined following the experimental procedure indicated in section 2.2.

Figure 5 (A) shows the weight percentages of the different mercury species in the exhaust streams from both fuel and air reactors referred to the total mercury in the anthracite fed at the two temperatures tested. Note that in all the experiments performed, mercury balances closed between 80-95%. These values inside the interval proposed in order to consider the balance correct (70-130%) [25-27]. The analysis of the results should consider the different atmospheres present in fuel and air reactors. In the fuel reactor, coal gasification with steam takes place in the presence of the oxygen carrier (Fe-ESF). Therefore, mercury release in this reactor would be compared to that expected in a conventional coal gasification unit. According to thermodynamics, it would have been expected that mercury vaporized completely once coal was introduced into the fuel reactor. However, the first relevant result that can be extracted from Figure 5 (A) is that not all the mercury in coal was released during coal gasification in the fuel reactor. Only around half of the total amount in average was measured there. Another interesting fact that can be obtained from Figure 5 (A) is that the major species in the fuel reactor is Hg^0 (g).

The volatility of mercury is known to be influenced by several variables such as temperature, coal composition and atmosphere. Li et al., 2011 [27] analyzed the effect of these variables on mercury volatility and speciation in a detailed study testing five different Chinese coals commonly used in gasification units. They concluded that the most influencing variable on mercury volatility was temperature. At 800ºC they reported volatilities between 75-85%, depending on the type of coal, while at 1200ºC the volatility was around 95% for all the coals. According to their results, some mercury remained in the char at the different temperatures tested. The mercury content in the coals also affected mercury volatility. The authors reported and increase in volatility with the increasing mercury content in most of the conditions tested. Besides temperature and mercury content, mercury volatility was found to depend on the mode of occurrence of mercury. Mercury in pyrite was more difficult to release than mercury in more hydrophilic minerals [27-29]. Moreover, steam may inhibit mercury volatility compared to oxygen [28,30]. Other factors may affect mercury volatility, but in much lesser extent. This is the case of the residence time [27]. Results presented in Figure 5 (A) agree with some of the findings summarized above. The amount of mercury released from anthracite in the fuel reactor increased with temperature. It was 39.5% of the total mercury at 875ºC and 56.6% at 920ºC. This value of mercury release in the fuel reactor at the highest temperature corresponds to a low value of char conversion, around 13% as seen in Figure 3. The mercury content of the anthracite is high (Table

2) which would favor mercury volatility. However, a strong affinity of mercury for sulfide association has been reported for anthracites [31]. The pyritic sulfur content is around 0.5% of the total sulfur in this coal, which may contribute to inhibit mercury volatility.

The major presence of Hg^0 (g) in the fuel reactor is in accordance with thermodynamics, which points to Hg^0 as the main species in gasification flue gases. The percentage of mercury released as Hg^0 (g) in the fuel reactor increases with temperature. It has been observed that in gasification environments, the increase in temperature increased the percentage of oxidized mercury, especially when the chlorine content in coal was high [27]. Moreover, although there is some controversy about the effect of the iron species [17,32], iron ore and alumina compounds have been identified as promoters of the conversion of Hg^0 to $Hg^{2+}X$, where X is Cl_2 or O [33]. However, the effects described above are not observed in the present experiments, as the molar ratio Hg^0/Hg^{2+} in the gas phase was 76/24 at 875ºC and 86/14 at 920ºC. The chlorine content in anthracite according to Table 2 was 183 mg/kg. The fuel reactor bed consists of Fe-ESF whose major constituents are Fe_2O_3 and Al_2O_3. In principle, the presence of this oxygen carrier may contribute to a larger extent of mercury oxidation when compared to conventional gasification, although in this case the surface area of the Fe-ESF material is low (0.1 m^2/g). However, the effect of both the increase in temperature and the presence of Fe-ESF seem to be hindered by the SO_2 present in the flue gases of the fuel reactor. As mentioned before, SO_2 can inhibit mercury oxidation if high amounts of chlorine are present in the flue gases [21]. This may be the case in these experiments. At 920ºC, around 6600 ppm of SO_2 were detected at the outlet of the fuel reactor and the amount of SO_2 is expected to increase with temperature, as the transformation of H_2S to SO_2 is favored by temperature [10]. Following this SO_2 inhibition tendency, the extent of

Hg^0 reduction would decrease with the increase in the fuel reactor temperature, as it was observed in Figure 5 (A).

Following the previous results, Figure 5 (A) shows the mercury emitted in the air reactor at the two fuel reactor temperatures analyzed. In the air reactor, air is introduced to regenerate the oxygen carrier. The char transported to this reactor will be also burned here in the reaction with air. Thus, mercury emissions in the air reactor would be comparable to those obtained in a conventional combustion system such as pulverized coal fired boiler. Measurements performed in several coal combustion pilot- and full-scale systems before the air pollution control devices (APCD) showed that the gaseous and particulate Hg^{2+} compounds, $Hg^{2+}X$ (s,g), generally represent more than half of the total mercury present in combustion flue gases. The other predominant form of mercury in combustion flue gas is Hg^0(g) [14]. In the present experiments, the temperature in the air reactor was maintained constant at 950ºC. It can be assumed that at this temperature almost all of the mercury was released, as no mercury was found in the fly ash escaping from the air reactor (Hg_AR,s). The amount of mercury released in the air reactor gases decreases with the increase in the fuel reactor temperature as more mercury had been previously released in the fuel reactor. The mercury released in the air reactor represents 40.5% of the total mercury at 875 ºC and 38.7% at 920ºC. The mercury speciation found in the air reactor was also presented in Figure 5 (A). In this case, the molar ratio Hg^0/Hg^{2+} was 38/62 at the two fuel reactor temperatures. Oxidized mercury is the major species. The presence of significant excess oxygen would favor mercury catalytic oxidation. Although SO_2 was also detected in the air reactor flue gas, the amount was around 100 times less than that found in the fuel reactor. Therefore, no inhibition effect of this gas on mercury oxidation is expected.

In order to further evaluate mercury emissions in CLC systems, the measurements using Fe-ESF and anthracite were compared to those obtained in the same experimental unit using ilmenite as oxygen carrier and Spanish lignite as fuel [10]. The mercury content in the lignite used was 0.11 mg/kg and the chlorine content was 63 mg/kg, both less than in the case of anthracite. The mercury content in ilmenite was negligible. The temperature for the experiment performed with lignite was an intermediate temperature between those used with anthracite, i.e. 910ºC.

The comparison of mercury measurements at the outlet stream of fuel and air reactors using lignite is shown in Figure 5 (B). Regarding mercury emission in the fuel reactor, the first important result in the experiments with lignite is that only around of 31.5% of the mercury in the coal was emitted, although char conversion reached 87%. This value was lower than 39.5% found in the experiments with anthracite at 875ºC and in this case, char conversion was 7%. According to this, char conversion does not seem to affect mercury release. Temperature would be the key variable influencing mercury volatilization. But according to this, higher mercury release would be expected in the experiments with lignite at 910ºC. The lower value found can be explained considering several factors. First, the larger mercury content of the anthracite compared to lignite and especially, the higher content of pyritic sulfur in the lignite used (1.9 wt.% in the coal) which would notably difficult mercury volatilization. The residence time of the coal particles in the fuel reactor was also shorter in the experiments with lignite, but the difference is not significant enough to justify the decrease in mercury volatility. The molar ratio Hg^0/Hg^{2+} in the fuel reactor was calculated and resulted 75/25. It is interesting to highlight that the major mercury species in the fuel reactor atmosphere was again Hg^0 (g). Important mercury oxidation inhibition by SO_2 would also be expectable in the experiments with lignite, as the concentration of this gas in the fuel rector was very high [10]. In the oxidizing environment of the air reactor, Hg^{2+} was again the most abundant species. The molar ratio Hg^0/Hg^{2+} measured in the air reactor was 46/54.

The analysis of mercury release with different coals, such as anthracite and lignite allow to draw some interesting conclusions for the *i*G-CLC process. From the findings presented above it can be expected that mercury in coal will be split and released both in fuel and air reactors. The split ratio will mainly depend on the type of coal used and foremost on the fuel reactor temperature. The main species that could be found in the fuel reactor would be Hg^0(g) while in the air reactor the predominant species would be Hg^{2+}(g).

4. Mercury emissions and CO_2 quality

The results shown are relevant for addressing Hg emission control in the CLC system and also regarding the quality of the CO_2 obtained. The identification and quantification of Hg speciation forms is important as Hg^0 and Hg^{2+} have distinctive physical, chemical and biological properties [14]. Mercury emission to the atmosphere may take place in the air reactor while the mercury released in the fuel reactor will be present in the CO_2 stream intended to be captured

Directive 2010/75/UE sets the limits for mercury emissions from incineration systems to 0.05 mg/Nm^3 (normalized to 10% O_2 vd. in the outlet stream). In the absence of specific limits for combustion systems, this value can be taken as a reference. Table 3 gathers the emission values measured in the air reactor in the different experiments presented in this paper. Mercury emissions in the air reactor are well below the 0.05 mg/Nm^3 and would not be a problem in CLC systems, even in the case of using coals with high mercury content like the anthracite used in this work. In the case that the outlet stream from the air reactor should be treated to control other emissions like NO_x, particulate matter or sulfur emissions, mercury emission could even be reduced. It has been already reported that combustion systems equipped with SCR, ESP and wet FGD significantly contribute to increase mercury removal efficiency [25].

On the other hand, the mercury released in the fuel reactor affects CO_2 quality. In the past years, several studies have addressed the analysis of the quantities of other compounds that may be present in a CO_2 stream intended for capture and storage. The presence of these compounds can affect energy requirements in transport and storage. De Visser et al. [34] presented some recommendations for pipeline CO_2 transportation. In these recommendations no values for mercury were included, although it is already known that the presence of trace elements can cause important operational problems related to liquid metal embrittlement in the aluminium components. There are three different levels where mercury, both elemental and ionic, could be captured in the CO_2 processing unit: the compression stage, the moisture removal stage and by activated carbon injection (ACI), which has revealed as one of the most promising options for mercury removal [18]. Activated carbon beds have been commonly employed in the natural gas industry to reach concentrations less than 0.01 µg/m^3, which is the limit settled to avoid operational problems. Table 3 also includes the total concentration of mercury that was measured in the fuel reactor in the experiments with different fuels. Real CLC systems will include a carbon separation unit, where unconverted char from the fuel reactor would be separated from the oxygen carrier particles and returned back to the fuel reactor. The char would therefore increase the residence time in the fuel reactor. It is expected that the carbon separation unit improves the carbon capture efficiency of the process but regarding mercury emissions, no important effect is foreseen as the increase in the residence time has not a great effect on mercury volatility at a certain temperature. The mercury content measured in the fuel reactor outlet (dry basis) was much larger than that demanded in order to avoid corrosion problems in the pipelines. Therefore, it can be anticipated that the CO_2 stream from the fuel reactor should be treated to reduce its mercury content.

The results obtained in this work allow us to predict that the release of mercury in a CLC system will be more an operational than an environmental issue. In a CLC system, mercury emissions will be significantly reduced compared to conventional combustion as only the mercury released in the air reactor will be emitted to the atmosphere.

5. Conclusions

Mercury release in a continuous *i*G-CLC unit using anthracite and lignite as fuels and low cost Fe-based oxygen carriers was analyzed. The mercury content in the solids in the system and the gaseous streams exiting from both fuel and air reactor was measured. The influence of operating parameters was evaluated, mainly the fuel reactor temperature, which was varied between 875 and 930ºC.

It was found that the amount of mercury released in the fuel reactor depended mostly on the fuel reactor temperature and the coal used. Values around 39.5 and 56.6% of the total mercury were found in experiments with anthracite. The increase in temperature resulted in an increase of the amount of mercury released in the fuel reactor. However, a high pyrite content of the coal negatively affected mercury volatility.

Mercury speciation was also measured as it is the key factor determining the mercury control measurements to adopt. In the fuel reactor, Hg^0 was found to be the major species. In this case, it is speculated that the high SO_2 concentration in the experiments with anthracite and lignite may play some inhibition effect on elemental mercury oxidation to Hg^{2+}. In the air reactor, with oxidizing conditions, mercury will be found mainly as Hg^{2+}.

Considering the total mercury concentrations at the outlet of both reactors found in this work, no problems with mercury emissions in the air reactor are anticipated if the legislation corresponding to incineration systems is considered as reference. Nevertheless, the mercury content in the fuel reactor outlet stream should be reduced to avoid operational problems in the CO_2 processing unit.

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Nomenclature

$F_{CO_2,AR}$: carbon dioxide molar flow in the air reactor (mol/s)

$F_{C,vol}$: carbon flow from the volatile matter (mol/s)

$F_{i,\ FR}$: *i* species molar flow in the fuel reactor inlet/outlet stream (mol/s)

F_{OC}: solid circulation rate (kg/h)

M_{O_2} : molar mass of molecular oxygen (0.032 kg/mol)

$\dot{m}_{SF}$: coal mass flow (kg/s)

R_{OC}: oxygen transport capacity (%)

X_{char}: char conversion

Greek symbols

ϕ: oxygen-carrier to fuel ratio

Ω_{SF}: coal oxygen demand (kg oxygen/kg coal)

Ω_T: total oxygen demand (%)

η_{CC}: carbon capture efficiency

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List of Figure captions

Figure 1. Reaction scheme of the *i*G-CLC process

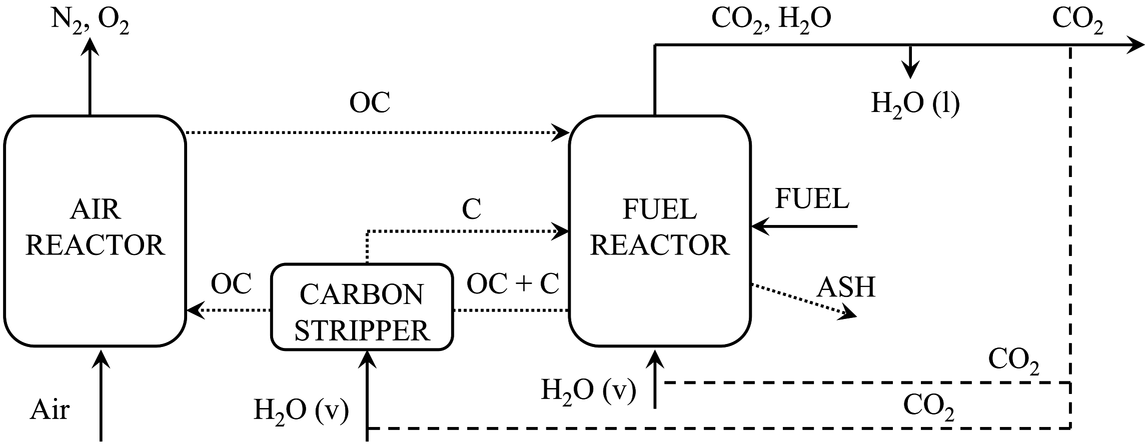
Figure 2. Evolution with time of the gas concentration (dry basis and N_2 free) of the main gases in the fuel reactor (CO, CO_2, H_2, CH_4, SO_2 and Hg^0/Hg^{2+}) and in the air reactor (O_2, CO_2, SO_2, Hg^0/Hg^{2+}) at T_{FR} = 920ºC

Figure 3. Carbon capture efficiency (η_{CC}) ■, char conversion (X_{char}) Δ and total oxygen demand (Ω_T) ● in experiments at different FR temperatures. Conditions : $\phi = 1$

Figure 4. Scheme of the continuous rig and the streams where mercury measurements were performed. FR: fuel reactor; AR: air reactor; g: gas; s: solid

Figure 5. Total mercury emissions in FR and AR at different temperatures referred to the total mercury in the coal fed in the experiments with (A) anthracite and (B) lignite

Figures



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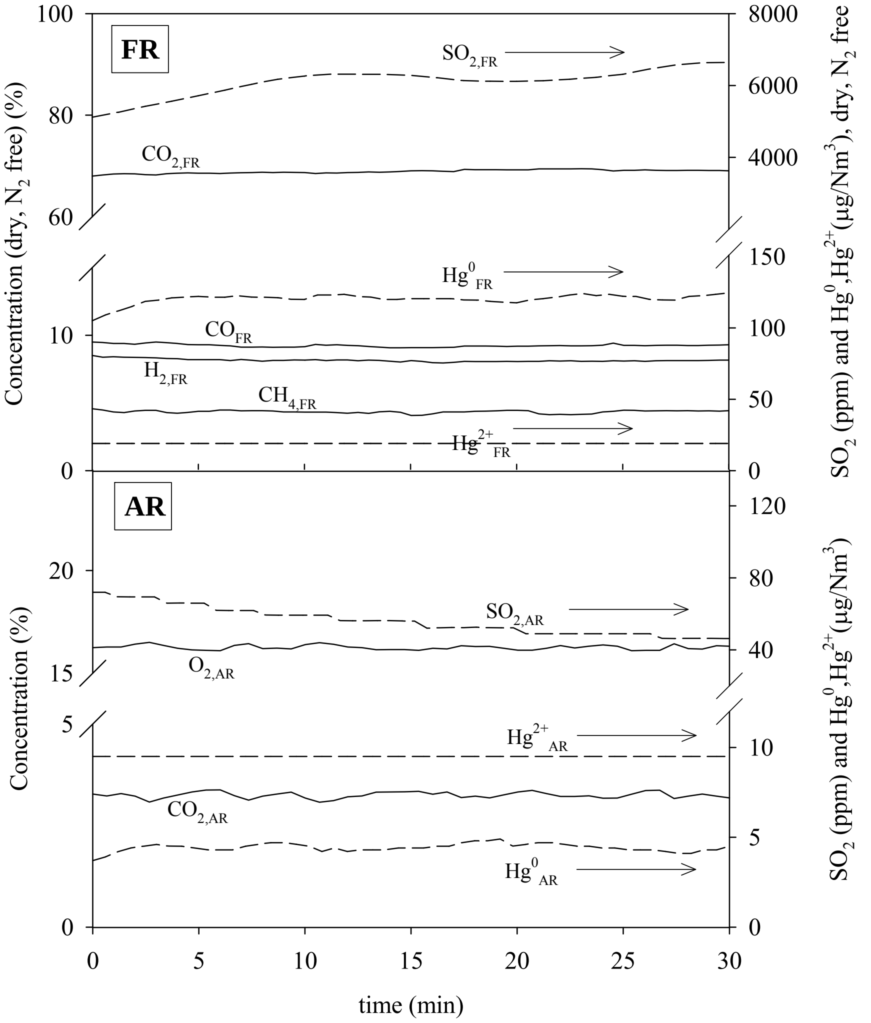

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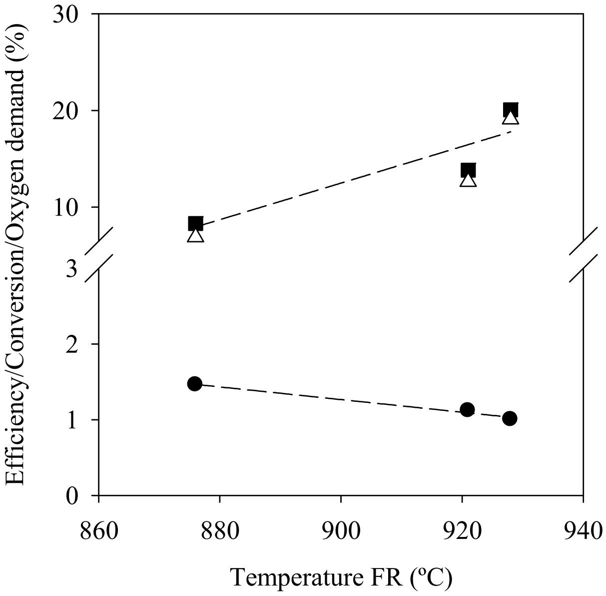

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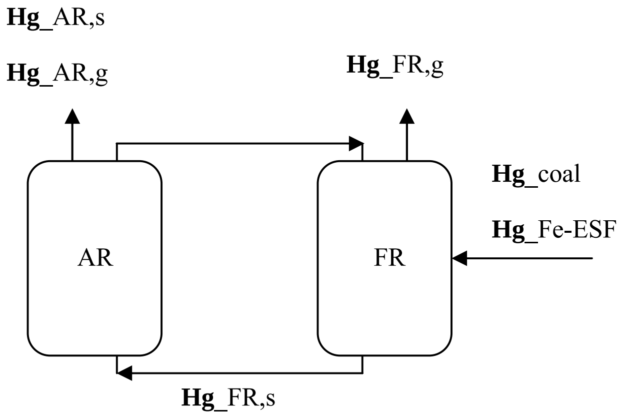

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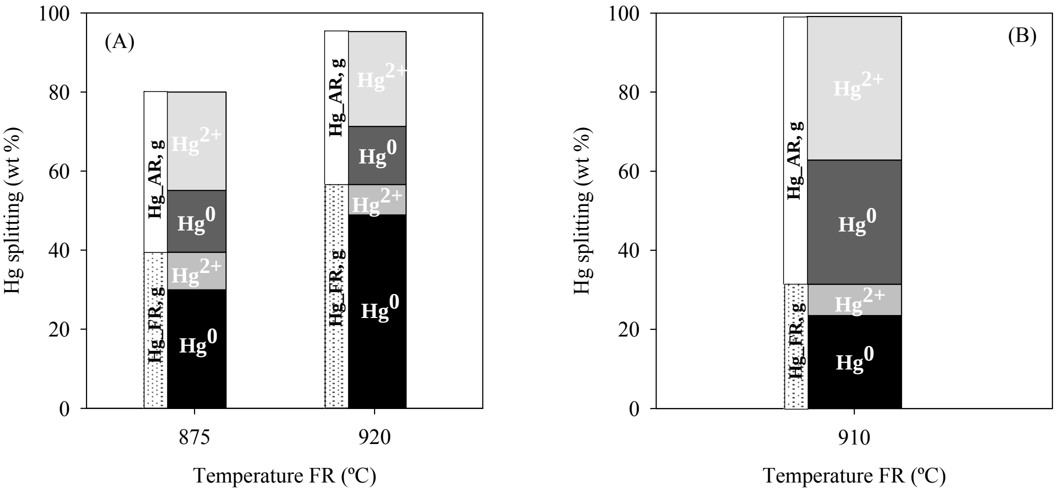

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Tables

Table 1. Characterization of the bauxite waste

Fe_2O_3 (wt. %) [a]	58
XRD main phases	Fe_2O_3, β-Al_2O_3
Crushing strength (N)	4.3
Oxygen transport capacity, R_{OC} (%)[b]	2
Porosity (%)	10
Skeletal density (kg/m^3)	4266
Specific surface area, BET (m^2/g)	0.1

[a] Determined by TGA

[b] Transformation to Fe_3O_4

Table 2. Proximate and ultimate analysis of the anthracite and lignite used (% wt except indicated)

Elemental (wt.%)	Anthracite	Lignite	Proximate (wt.%)	Anthracite	Lignite
Carbon	60.7	45.4	Moisture	1.0	12.5
Hydrogen	2.0	2.5	Ash	31.5	25.2
Nitrogen	0.9	0.6	Volatile matter	7.5	28.6
Sulfur	1.3	5.2	Fixed carbon	59.9	33.6
Oxygen[a]	2.7	9.9			
Mercury (mg/kg)	0.274	0.108			
Chlorine (mg/kg)	183	63			
LHV (kJ/kg)	21878	16251			

[a] By difference

Table 3. Mercury concentration in the fuel and air reactors in *i*G-CLC experiments with different fuels

Coal	**T_{FR} (ºC)**	**Hg_{FR} (mg/Nm^3)**	**Hg_{AR} (mg/Nm^3) (10% vd.)**
Anthracite	875	0.082	0.006
	920	0.084	0.005
Lignite	910	0.015	0.011