Sulphur, nitrogen and mercury emissions from coal combustion with CO₂ capture in Chemical Looping with Oxygen Uncoupling (CLOU)

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Abstract – Chemical Looping with Oxygen Uncoupling (CLOU) is a Chemical Looping Combustion (CLC) process that allows the combustion of solid fuels through the use of a solid oxygen carrier that release gaseous oxygen inside the fuel reactor. The aim of this work was to study the fate of elements potentially pollutant present in fuel during CLOU combustion, i.e. S, N and Hg. Experiments using lignite as fuel were carried out in a continuously operated 1.5 kW_{th} CLOU unit during more than 35 h of coal combustion. Novel particles containing 50 wt. % CuO, 10 wt. % Fe₂O₃ and 40 wt. % MgAl₂O₄, prepared by spray drying, were used as oxygen carrier in the CLOU process. The temperature in the fuel reactor varied between 885 and 945 °C. Both the reactivity and oxygen transport capacity of the oxygen carrier were unaffected during operation with a high sulphur content fuel, and agglomeration problems did not occur. Complete combustion of the fuel to CO₂ and H₂O was found in all experiments. Sulphur, NO_x and Hg emissions from fuel and air reactor streams in the process were analyzed. Most of the sulphur introduced with the fuel exited as SO₂ at the fuel reactor outlet, although a small amount of SO₂ was

measured at the air reactor outlet. Most of the nitrogen present in coal was found as N_2 at the outlet of the fuel reactor, but 20 wt. % of N in coal was converted to NO. NH_3 , HCN or N_2O were never detected. In the air reactor, small amounts of NO were detected due to the nitrogen contained in unburnt char transferred to this air reactor. Mercury speciation was also analyzed. In the fuel reactor the major mercury specie was Hg^0 (g) and in the air reactor the ratio Hg^0 (g) / Hg^{total} (g) was 0.5.

Keywords: CLC, CLOU, CO_2 capture, coal, pollutant emissions.

1 Introduction

In order to stabilize the CO_2 concentration in the atmosphere several measures must be taken. Among them, Carbon Capture and Storage (CCS) would contribute with 15–55% to the cumulative mitigation effort worldwide until 2100 [1]. New technologies have been developed to facilitate CO_2 capture and storage (CCS). Chemical Looping Combustion (CLC) is a promising CCS technology which allows CO_2 capture from power plants at low cost [2]. There are two options to burn a solid fuel in a CLC system. In the first, the solid fuel is gasified *in-situ* in the fuel reactor using steam or CO_2 as fluidization agents and the oxygen carrier particles oxidized the gaseous products of coal devolatilization/gasification and char to CO_2 and H_2O (*iG*-CLC). In the second option, known as Chemical Looping with Oxygen Uncoupling (CLOU), the solid fuel is burned with the gaseous oxygen released through the oxygen carrier in the fuel reactor [2, 3].

In the *i*G-CLC process the solid fuel must be gasified at the fuel reactor. The gasification reaction is slow and part of the unreacted char exits from the fuel reactor [4, 5], thus requiring the use of a carbon stripper to re-circulate the unconverted char to the fuel reactor [6]. Also, there are always unburnt products at the fuel reactor gas outlet [7].

The Chemical Looping with Oxygen Uncoupling (CLOU) is a type of Chemical Looping Combustion (CLC) technology that allows the combustion of solid fuels with inherent CO₂ separation using oxygen carriers. CLOU technology takes advantage of the property of some metal oxides for generating gaseous oxygen at high temperatures, e.g. 800-1000 °C, and may be particularly suitable for solid fuels, such as coal and biomass. The oxygen generated by the oxygen carrier reacts directly with the solid fuel, which is mixed with the oxygen carrier in the fuel reactor. The oxygen carriers for CLOU must first have the ability to release this oxygen through decomposition inside the fuel reactor, and then to regenerate with oxygen in the air reactor following the scheme in Fig. 1. Low cost materials based on Fe [2, 5, 6] or CaSO₄ [8, 9] has been proposed for the *i*G-CLC process. However, only metal oxide systems based on Cu, Mn or Co were found to be suitable as oxygen carriers in the CLOU process [3], but the combustion of solid fuels by the CLOU process has been found to have better performance than the *i*G-CLC [10]. Peltola et al. [11] carried out mass, energy, and exergy balances of a CLOU system with CuO-based oxygen carrier and found that the possible operating conditions in the system are closely related to the properties of the chosen oxygen carrier. In this way, oxygen carrier

inventories of 400–680 kg/MW in the system were found necessary for stoichiometric combustion of the fuel.

Fig. 1. Schematic diagram of the CLOU process, including the possible fate of S, N and Hg elements.

Mattisson [12] reviewed the materials proposed to be used in CLOU, including oxygen carriers based on Cu [13, 14], and mixed oxides of Cu-Mn, Mn-Fe and Mn-Si [15]. However, in the literature only a Cu-based material has been tested with solid fuels in a continuous unit. Particles of 60 wt.% CuO prepared by spray drying were tested in a 1.5 kW_{th} CLOU continuous unit [16], where proof-of-the-concept of the CLOU process was demonstrated using coal as fuel. The effect of the coal rank on the process performance was also analysed [17] in this plant using a lignite, two bituminous coals and an anthracite. Moreover, biomass combustion was tested with encouraging results [18]. It has been found that CLOU process with CuO oxygen carriers allows complete combustion of coals

of any rank (from anthracite to lignite) and biomass [16-18] with also high CO₂ capture efficiency.

Once the feasibility of the CLOU concept was demonstrated burning coal, pollutant emissions must be also analyzed. Considering coal as fuel, there are some compounds which could be present as impurities in the CO₂ stream and/or pollutant emitted to the atmosphere if corrective actions are not implemented. From the operational perspective of CLOU process, there are three main pollutant species to take into account: SO_x, NO_x and Hg. In CLC and CLOU units the fate of pollutant compounds is more complex than in common coal combustion with air because the existence of two separated gaseous streams from the process; see Fig. 1. From the environmental perspective, pollutant can be released from the air reactor, and so there must be fulfil the legislation governing gaseous emissions [19]. SO₂ and NO_x compounds (NO, NO₂ and N₂O) could be formed by the oxidation of the nitrogen compounds present in coal. These compounds are acid rain precursors. Moreover, NO_x are greenhouse gases and they are participated in the production of photochemical smog. Hg could appear during the combustion as three species Hg⁰(g), Hg²⁺(g) and particle-bong mercury Hg(p). The oxidized specie can be removed from the effluent gases during a wet desulphurization due to the high solubility of this compound. On the other hand, Hg⁰(g) is more difficult to remove due to the high vapour pressure and low water solubility [20]. Moreover, this compound remains stable at the atmosphere after the emission and can enter to the food chain with the risk to affect to the human health [20].

In addition, S, N and Hg can also be emitted in the fuel reactor gas stream as impurities, thereby affecting the quality of the CO₂ and with important consequences for its compression, transport and storage [21, 22]. Pipitone and Bollard [23] give some examples of quality specifications for CO₂ transport and storage of some industrial companies currently in force. The Dynamis project [24] tries on specified the CO₂ stream quality for transport and storage. Table 1 shows the maximum values for the different pollutant compounds that could be present in the CO₂ stream. It can be seen that the maximum pollutant concentration for SO_x and NO_x compounds is of 100 ppm. Furthermore, the mercury that exit in the fuel reactor gas stream will affect to the CO₂ quality. Hg⁰ (g) can be accumulated in the CO₂ processing unit and affect to the aluminium heat exchanges. Also, the presence of mercury in the CO₂ stream can produce undesired reactions as mineralization and/or precipitation in the condition of CO₂ stream operation [25].

Finally, S compounds may react with the active metal oxide to form metal sulphides or sulphates, which can be detrimental to the oxygen carrier, decreasing its reactivity. Moreover, the low melting point of some S compounds, e.g. 1100 °C for Cu₂S, could produce agglomerations and to affect the solid circulation pattern between the interconnected fluidized-bed reactors.

Table 1. Maximum values for main pollutant compounds in the CO₂ stream of Dyamis project [24].

Compound	Maximum values (ppm)
H ₂ O	500
H ₂ S	200
CO	2000
SO _x	100
NO _x	100

3

4

5 Up to date, little attention has been paid in the S, N and/or Hg compounds in
6 gases exiting in the use of coal in *i*G-CLC or CLOU. Mendiara et al. [26] studied
7 the emission of sulphur compounds in *i*G-CLC process with ilmenite as oxygen
8 carrier, burning a lignite with high amount of sulphur in its composition in a
9 temperature range between 875-930 °C. They obtained that a 90% percent of
10 the sulphur in the coal exits from the fuel reactor as H₂S and SO₂, without COS
11 or CS₂. The presence of H₂S decreased when the temperature increased. In the
12 air reactor, the SO₂ concentration decreased with the fuel reactor temperature
13 because the increase of the char conversion in fuel reactor. Linderholm et al.
14 [27] also studied the pollutant emission during combustion of a bituminous coal
15 by *i*G-CLC process in a 100 kW_{th} continuous unit during 15 h with ilmenite as
16 oxygen carrier. They observed that the 72% of the sulphur feed to the system is

converted in the fuel reactor. Distribution of sulphur compounds present in the fuel reactor gas outlet, was 75% SO₂ and 25% of H₂S [27].

Respect to the NO_x emissions, Mendiara et al. [26] found that for *i*G-CLC process around the 99 vol.% of the nitrogen measured in the fuel reactor was as N₂, the only NO_x compound detected was NO, with traces of NO₂, NH₃ and HCN. There was not N₂O at the fuel reactor exit. In the air reactor, only NO has been detected (without traces of N₂O or NO₂) and the amount depends on the unconverted char transferred to the air reactor, which agrees to results obtained in a 1 kW_{th} prototype with an iron ore as oxygen carrier [28-30]. Moreover, the gasification medium used in the fuel reactor affect to the NO yield in the air reactor, being lower when H₂O instead of CO₂ was used [29]. However, different results were found in these works regarding the presence of nitrogen oxides in the fuel reactor. Thus, no N-compound other than N₂ was found in [28], but also NO or N₂O+NO was found in [29] and [30], respectively. Likely, the high concentration of H₂, CO and CH₄ obtained in fuel reactor in [28] reduced NO to N₂. On the contrary, Linderholm et al. [27] also found HCN and NH₃ in gases from the fuel reactor, being the 62% of nitrogen in coal converted to gaseous N, distributed as 1 wt.% of HCN, 11 wt.% NO, 26 wt.% NH₃ and the rest N₂.

Regarding Hg emissions, Mendiara et al. [26, 31] studied the Hg emissions from the fuel and air reactors in a *i*G-CLC process burning a lignite and an anthracite. They observed that the temperature could be the key influencing mercury

1 volatilization. Mercury oxidation inhibition in the experiments done with lignite
2 was observed due to the high concentration of SO_2 present in the fuel reactor
3 atmosphere. They concluded that the mercury present in the coal will be
4 distributed in both fuel and air reactor exit streams. The split ratio depended on
5 the fuel reactor temperature and the coal used. Mainly, it will be expected that
6 Hg^0 (g) will be the major specie at the fuel reactor outlet and Hg^{2+} (g) at the air
7 reactor.

8
9 Up to day, for the CLOU process burning a solid fuel, there are few works about
10 pollutant emissions. Adánez-Rubio et al. [32] focussed on sulphur emissions,
11 studied the fate of the sulphur in a continuous CLOU unit using a Cu-based
12 oxygen carrier and a lignite with high amount of sulphur as fuel (5.2 wt.%). They
13 found that a 88 wt.% of the sulphur in the effluent gases exit from the fuel
14 reactor as SO_2 . Some SO_2 exit from the air reactor which comes from the
15 unconverted char transferred to the air reactor together with the pyritic sulphur
16 present in the coal ashes of this lignite (2 wt.% in the coal). Around 20 wt.% of
17 sulphur was not detected, and the reason for it was unclear. Respect to NO_x
18 emissions, Song et al. [33] studied the nitrogen conversion of the fuel in a batch
19 fluidized bed reactor with different solid fuels using a Cu-based oxygen carrier
20 for CLOU. The experiments were done using N_2 as fluidizing agent during the
21 fuel combustion, which can affect to the NO_x formation [26]. They found an
22 important amount of NO_2 together with NO , and also they detected N_2O when
23 they burnt coal. There are not any other studies about the emissions of Hg for
24 CLOU process available in the literature.

The aim of this work was to investigate the emissions of sulphur, nitrogen and mercury compounds in the CLOU process using a novel Cu-Fe oxygen carrier. The experiments were conducted using a Spanish lignite with a high S content in a 1.5 kW_{th} continuous unit. The effect of fuel reactor temperature on the combustion efficiency, carbon capture efficiency and sulphur, NO_x and Hg emissions was studied. The results obtained are analysed and discussed in order to identify potential problems in the industrial operation of the CLOU process.

2 Experimental section

2.1 Oxygen carrier

The oxygen carrier was a Cu-Fe material prepared by spray drying. Oxygen carrier particles were manufactured by VITO (Flemish Institute for Technological Research, Belgium) using a mixture of 10 wt. % of Fe₂O₃ and 40 wt. % of MgAl₂O₄ as inerts. The CuO content was 50 wt. %. The particles were calcined in air during 12 hours at 1075 °C. The particle size of the oxygen carrier was +0.1-0.3 mm. The content of mercury in the oxygen carrier was 1.1 10⁻⁴ mg Hg/kg. The main properties of this oxygen carrier are summarized in Table 2. The oxygen transport capacity, R_{OC} , was calculated regarding the conversion during the oxygen uncoupling reaction. However, some CuO formed CuFe₂O₄ compound, which was unreactive for the oxygen uncoupling reaction. Thus, the active CuO was 45 wt. %. From now on, the oxygen carrier was named as Cu50Fe/MgAl.

1

2 **Table 2.** Main properties of Cu50Fe/MgAl particles.

Oxygen transport capacity ^a (wt. %)	4.5
Crushing strength (N)	2.6
Porosity (%)	21.4
Skeletal density (kg/m ³)	4547
Specific surface area ,BET (m ² /g)	<0.5
XRD main phases	CuO, CuFe ₂ O ₄ , MgAl ₂ O ₄

3

^adetermined by TGA in N₂

4

5 **2.2 Fuel**

6 A Spanish lignite from Teruel basin (+0.2-0.3 mm) was used as fuel in the
7 experiments. Table 3 shows the proximate and ultimate analyses of the lignite,
8 with a LHV value of 16250 kJ/kg. The content of mercury in the lignite was
9 0.108 mg Hg/kg.

10 **Table 3.** Properties of lignite as received basis.

Lignite			
Moisture (%)	12.6	C (%)	45.4
Volatile matter (%)	28.6	H (%)	2.5
Fixed carbón (%)	33.6	N (%)	0.6
Ash (%)	25.2	S (%)	5.2

	O (%) ⁽¹⁾	8.5
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⁽¹⁾Oxygen to balance.

2.3 Experimental set-up

Coal combustion experiments were performed at the ICB-CSIC-s1 unit, previously used in other investigations from our research group [16-18, 32]. The diagram of the setup is presented in Fig. 2. This experimental unit was composed of two interconnected fluidized bed reactors, (1) and (3) in Fig. 2, electrically heated by their corresponding furnaces (11). The fuel reactor (1) and the air reactor (3) are connected by a fluidized bed acting as loop seal (2), a riser (4) for solids transport from the air to the fuel reactor and a cyclone to recover the entrained solids (5).

The fuel reactor consisted of a bubbling fluidized bed (50 mm ID and 200 mm bed height). Coal is fed by a screw feeder (10) at the bottom of this bed and above the fuel reactor distributor plate in order to maximize the time that volatile matter is in contact with the oxygen carrier in the bed. In order to avoid gas backflow from the fuel reactor, a small gas flow was introduced to the screw feeder. In the fuel reactor, the oxygen carrier is reduced by coal.

Fig. 2. Experimental unit ICB-CSIC-s1.

The reduced oxygen carrier particles overflow through a U-shaped fluidized bed loop seal (50 mm ID) to the air reactor, avoiding mixing gaseous atmospheres between fuel and air reactors. Preliminary results showed that about 50% of the N_2 introduced to fluidize the loop seal derived to the fuel reactor and the rest to the air reactor. The reduced oxygen carrier is oxidized in the air reactor (80 mm ID and 100 mm bed height). Secondary air was introduced at the top of the bubbling bed to help particle entrainment. The outlet stream from the air reactor was sent up the riser to the stack through a high-efficiency cyclone and a double filters system. The oxidized oxygen carrier particles recovered by the cyclone were sent to a solid reservoir (7) which acts as a loop seal avoiding the

leakage of gas between the fuel reactor and the riser. The solid flow rate of regenerated oxygen carrier to the fuel reactor was controlled using a solid valve placed in the solid reservoir. A diverting solid valve (6) allowed the measurement of the solids flow rates at any time. A solid valve (8) controlled the solid flow fed to the fuel reactor.

CO, CO₂, H₂, CH₄ and O₂ concentration in the fuel reactor outlet stream and CO, CO₂ and O₂ from the air reactor were continuously recorded. Different analyser's systems were used for gas concentration measurements in the fuel reactor. For CH₄, CO and CO₂ nondispersive infrared (NDIR) analysers (Maihak S710/UNOR and Siemens Ultramat 23) were used; a paramagnetic analyzer (Maihak S710/OXOR-P and Siemens Ultramat 23) was used for O₂ concentration measurement and a thermal conductivity detector (Maihak S710/THERMOR) was used for H₂. The analysis of sulphur and nitrogen species required different equipment. H₂S and COS were measured using a gas chromatograph and SO₂ using an infrared Siemens Ultramat 23 analyzer. Nitrogen compounds (N₂, NO, NO₂, N₂O, NH₃ and HCN) were measured with a quadrupole mass spectrometer from Pfeiffer. The amount of tar present in the fuel reactor product gas was determined following the tar protocol [34]. Higher C₂, C₃ and C₄ hydrocarbons were analysed off-line by a gas chromatograph (HP5890 Series II). Respect to mercury species, oxidized mercury (Hg²⁺ (g)) was retained in KCl impingers with a solution 1 M of KCl placed in a bath at 0 °C (Ontario Hydro Method). The Hg²⁺(g) together with Hg (p) retained in solid streams were measured by gold amalgam atomic absorption spectroscopy

(LECO AMA254). Hg^0 (g) was analyzed by cold vapour atomic absorption spectroscopy (CVAAS VM3000 from MCI). Since SO_2 affects CVAAS signal, the analyser was previously calibrated with different SO_2 concentrations in order to subtract its contribution during Hg^0 (g) measurement.

To investigate the combustion efficiency in fuel reactor, CO_2 capture efficiency in the process, and S splitting between reactors, the fuel reactor was fluidized with N_2 . However, during the tests to investigate N splitting, CO_2 was used as fluidizing agent in the reactor and loop seal. Thus, N-fuel was the only source for N-compounds at the fuel reactor exit stream. The fuel reactor temperature was varied between 885 °C and 945 °C. The temperature in the air reactor was kept at around 900 °C in all experiments. The gas flow to the fuel reactor (N_2 or CO_2) was 250 $\text{L}_\text{N}/\text{h}$, which correspond to a linear gas velocity of 0.15 m/s at 900 °C. In the air reactor the total primary air flow was 1740 $\text{L}_\text{N}/\text{h}$ (corresponding to a gas velocity of 0.4 m/s at 900 °C). The secondary air flow was 240 $\text{L}_\text{N}/\text{h}$. Considering both primary and secondary air flows, the gas velocity in the riser was 3.3 m/s. The gas flow in the loop seal was 60 $\text{L}_\text{N}/\text{h}$. The solids circulation rate was kept at a mean value of 3.8 kg/h, whereas the coal feeding rate was 0.13 kg/h, which corresponded to an oxygen carrier to fuel ratio, ϕ , of 1.1. The oxygen carrier to fuel ratio was defined as the ratio of the oxygen transported by the oxygen carrier to the oxygen demanded by coal for complete combustion. A value of $\phi = 1$ corresponded to the stoichiometric flow of CuO needed to fully convert the fuel to CO_2 and H_2O , with CuO being reduced to Cu_2O . Thus, ϕ was calculated with the following equation:

1
$$\phi = \frac{R_{OC}\dot{m}_{OC}}{\Omega_{coal}\dot{m}_{coal}} \quad (1)$$

2 where $\dot{m}_{OC}$ is the solids circulation flow rate in the completely oxidized state and
3 $\dot{m}_{coal}$ is the mass-based flow of the solid fuel fed into the reactor. Ω_{coal} is the
4 stoichiometric kg of oxygen to convert 1 kg of coal to CO₂ and H₂O. This value
5 was calculated from the proximate and ultimate analysis of coal ($\Omega_{coal} = 1.3$ kg
6 O₂/kg coal), by using the following equation:

7
$$\Omega_{coal} = \left(\frac{f_C}{M_C} + 0.25 \frac{f_H}{M_H} + \frac{f_S}{M_S} - \frac{f_O}{M_{O_2}} \right) M_{O_2} \quad (2)$$

8 where f_i is the mass fraction of the element i in coal.

9

10 The solid inventory in the system was 2.5 kg, of which 0.45 kg was in fuel
11 reactor. This corresponds to 950 kg/MW_{th} in fuel reactor. During operation,
12 temperatures in the fuel, air reactor, and riser were monitored as well as the
13 pressure drops in selected points in the system. A total of 52 hours of hot
14 fluidization were carried out, of which 35 hours corresponded to coal
15 combustion.

16

17 **2.4 Data evaluation**

18 To analyze the performance of the CLOU process, the combustion efficiency in
19 the fuel reactor and the carbon capture efficiency were calculated. Calculations
20 were based on the molar flow of every gas analyzed, F_i , which was determined

from the measured concentrations. Mass balances were checked and a closing of around 96% was found for the C balance in all cases.

The combustion efficiency in the fuel reactor was calculated through the ratio between the oxygen required to fully burn unconverted gases (CH₄, CO and H₂) at the fuel reactor exit and the oxygen required by coal conversion in the fuel reactor. Thus, the oxygen required by the C bypassed to the air reactor was subtracted from the oxygen required by coal in the denominator. Therefore, the combustion efficiency in the fuel reactor was calculated as:

$$\eta_{\text{comb,FR}} = 1 - \frac{4F_{\text{CH}_4,\text{outFR}} + F_{\text{CO,outFR}} + F_{\text{H}_2,\text{outFR}} + 3F_{\text{H}_2\text{S,outFR}}}{\frac{1}{M_{\text{O}}} \Omega_{\text{coal}} n_{\text{coal}} - 2F_{\text{CO}_2,\text{outAR}} - 2F_{\text{SO}_2,\text{outAR}}} \quad (3)$$

The carbon capture efficiency, η_{cc} , is defined as the fraction of carbon present in the fuel at the outlet of fuel reactor. This is the real CO₂ captured in the CLOU system, as the remaining carbon exits as CO₂ together with nitrogen at the air reactor outlet:

$$\eta_{\text{cc}} = 1 - \frac{F_{\text{CO}_2,\text{outAR}}}{F_{\text{CO}_2,\text{outFR}} + F_{\text{CO,outFR}} + F_{\text{CH}_4,\text{outFR}} + F_{\text{CO}_2,\text{outAR}}} \quad (4)$$

The char conversion (X_{char}) is defined as the ratio between the carbon released in the fuel reactor and the fixed carbon in coal fed. Its value is calculated by considering that the carbon in gases from the fuel reactor comes from the carbon in volatiles and carbon in converted char. Thus, the carbon from reacting char was the inlet carbon minus the flow of carbon in volatiles, $F_{\text{C,vol}}$:

$$X_{\text{char}} = \frac{F_{\text{CO}_2, \text{outFR}} + F_{\text{CO, outFR}} + F_{\text{CH}_4, \text{outFR}} - F_{\text{C, vol}}}{F_{\text{CO}_2, \text{outFR}} + F_{\text{CO, outFR}} + F_{\text{CH}_4, \text{outFR}} + F_{\text{CO}_2, \text{outAR}} - F_{\text{C, vol}}} \quad (5)$$

With the molar flow of SO₂ and NO_x exiting from the air reactor and the total volume gas flow, the concentration of SO₂ and NO₂ as mg/Nm³ was calculated and normalized. EU legislation [19] requires the SO₂ and NO₂ concentration to be normalized using 6 vol.% O₂ in the exit stream for power plants.

3 Results and discussion

3.1. CLOU performance

During 35 h of lignite combustion operation, no CH₄ or H₂, were detected in the gases exiting from the fuel reactor. Neither tars nor hydrocarbons heavier than C₅, were detected at the outlet fuel reactor flow. Thus, CO₂ and H₂O were the main gas species exiting the fuel reactor. As unburnt products, a small CO amount were also detected at low fuel reactor temperature test (885°C). At temperatures higher than 900°C, the oxygen release rate of the oxygen carrier was high enough to supply an excess of gaseous oxygen (O₂) exiting together with the CO₂ and H₂O at fuel reactor outlet.

Regarding the fate of S and N during combustion, H₂S, NH₃, HCN, COS and CS₂ were never detected. Only SO₂ and NO+NO₂ were measured as the oxidized products coming from the S and N in coal at the fuel and air reactors outlets. Respect to mercury species, in both reactors were detected both Hg⁰ (g) and Hg²⁺ (g), with different distribution for each reactor. A deeper analysis of these species is done in a further section.

1

2 Fig. 3 shows the effect of the fuel reactor temperature on combustion and
3 carbon capture efficiencies. It can be seen that combustion efficiencies higher
4 than 99.6 % were always achieved. Moreover, the carbon capture efficiency
5 increased when the fuel reactor temperature increased because of an increase
6 in the char combustion rate. As volatiles are fully released in the fuel reactor,
7 the carbon capture only depends on the unconverted char transferred to the air
8 reactor, i.e. the char conversion. Besides, as it was previously found with a Cu-
9 based oxygen carrier [16, 17] and high reactivity coals, high CO₂ capture
10 efficiencies were reached. Also, it can be observed in Fig. 3 the values of char
11 conversion. The char conversion increased with the fuel reactor temperature
12 from 94.9% at 885 °C to 98.8% at 945 °C.

13

14

15 **Fig. 3.** Effect of fuel reactor temperature on char conversion (●), CO₂ capture
16 (▼) and combustion (◇) efficiencies in the fuel reactor.

3.2. Fate of sulphur in coal

In the fuel reactor, SO₂, H₂S, C₂S and COS could be present at the outlet stream. However, only SO₂ was detected as the sulphur specie at all the temperatures tested. SO₂ concentration (dry basis) measured at the fuel reactor outlet varied between 5080 vppm at 885 °C and 9190 vppm at 945 °C. In addition, some SO₂ was also present in the air reactor flue gas.

Fig. 4 shows the splitting of the total S fed in the continuous unit between gas and solid streams. A major S emission came from the fuel reactor stream in the form of SO₂ which increased with temperature. It can be seen that SO₂ emissions in the air reactor decreased with increasing temperature. This effect was due to more char being converted in the fuel reactor as the temperature increased with the corresponding decrease of the concentration of SO₂ in the air reactor outlet. These results are slightly different than those obtained in a previous work [32] burning this lignite with other Cu-based oxygen carrier. This is due to the higher oxygen carrier inventory in the fuel reactor in these tests (950 kg/MW_{th} in front of 844 kg/MW_{th}) that increase the char conversion in the fuel reactor (97.3 % to 97.9% at 925 °C), and increase the amount of SO₂ released from the fuel reactor (40.4% up to 57.3% at 950 °C).

Fig. 4. S splitting in the continuous CLOU plant. : fuel reactor gas outlet; : air reactor gas outlet; : self-retention by ashes; : pyritic S in ashes.

Fig. 5 shows the measured SO_2 emissions in the air reactor in normalized mg/Nm^3 as a function of the fuel reactor temperature. The EU SO_2 emission limits for new coal power plants ($>300 \text{ MW}_{\text{th}}$) are also depicted [19]. Although, the SO_2 distribution between fuel and air reactor streams at 945°C was 95/5 (wt.%), the value of the SO_2 emission was still too high and exceeded the EU legal limit of $200 \text{ mg}/\text{Nm}^3$ at 6% O_2 . As it has mentioned before, emissions of SO_2 in the air reactor come from combustion of char bypassed from the fuel reactor. Note that direct combustion of this coal with air would have produced SO_2 emissions of $> 20.000 \text{ mg}/\text{Nm}^3$.

Fig. 5. SO₂ emissions normalised at 6 vol.% O₂ in air reactor outlet stream at different fuel reactor temperatures. (♦) Measured SO₂ emissions; (▽) Calculated SO₂ emissions from char conversion; (---) EU legal emission.

Fig. 5 also shows the expected SO₂ emissions calculated from char conversion assuming a uniform C/S ratio during char combustion equal to the C/S ratio measured in char. As can be seen, these calculated SO₂ emissions are much lower than the measured ones. This fact could be due to two different effects: S was transferred to the air reactor in the oxygen carrier particles by S reaction with Cu or Fe, or S was concentrated in the unburnt char transferred to the air reactor. Adánez-Rubio et al. [32] analyzed the release of sulphur during coal combustion in CLOU and found that these high emissions may be due to a non-uniform S release during char combustion resulting from the presence of a high pyritic S content in this lignite (2 wt.%)

The S in the fuel and air reactor gas outlet was in the range of 53-63 wt.% of total sulphur in coal, as it can be seen in Fig 4. To determine the fate of the rest of the S fed with coal, solid streams coming from the fuel reactor and air reactor were also analyzed. S was also detected in the ashes in the form of pyritic S in both solid reactor streams. Around 10 wt.% of the total S fed was in the form of unburned pyritic S. Moreover, it is known that the presence of CaO in this lignite ashes enables the self-retention of S during combustion through the formation of CaSO_4 [35]. In this way, Fig. 4 also shows the amount of S in the ashes produced by self-retention (12 wt. % of the total S fed). Taking the S in gas and solid phases into account, the S balance closure was now at ~ 75- 85 wt. %.

3.3 Effect of the sulphur in the oxygen carrier

Due to the results obtained in the continuous unit respect to the global sulphur balance, some additional characterization tests were made. In the operating conditions existing in the fuel reactor (3 vol.% O_2) it is expected that S would be oxidized to SO_2 . A possible fate for the rest of S, not measured in both gas and solid streams, could be its accumulation in the oxygen carrier particles. In order to study the interaction of the SO_2 with the oxygen carrier, both TGA experiments and tests in a fluidized bed reactor were done at fuel reactor conditions using a fresh sample. A description of the TGA setup for high SO_2 concentrations and long operation time can be found in de las Obras-Loscertales et al. [36], while the fluidized bed reactor is described by Gayán et al. [14].

1

2 To simulate the fuel reactor conditions in the TGA experiment, a mixture of
3 reactive gases was used. This mixture contained: 3 vol.% of O₂, 8000 ppm of
4 SO₂ and N₂ to balance. 30 mg of fresh oxygen carrier Cu50Fe/MgAl were used
5 as sample. The duration of the experiment was 24 h at 930 °C. In these
6 conditions, thermodynamic calculations showed that CuSO₄ or (CuO)·(CuSO₄)
7 cannot be produced at temperatures higher than 700 °C [37]. CuSO₄ formation
8 would give a significant weight increase of the sample (around 50 wt. %). Thus,
9 in that conditions the weight of the sample must be stable, since CuO
10 decomposition is also not favored. However, after the test, the sample weight
11 increased a 12.8 wt. %, due to the reaction of the sample with the SO₂ fed.

12

13 Moreover, the oxygen carrier behavior in an atmosphere with high sulphur
14 concentration was analyzed in a batch fluidized bed reactor. In this test, 250 g
15 of fresh oxygen carrier were fluidized with a mixture of N₂ and 3000 vppm of
16 H₂S (275 L_N/h) at 925 °C, to observe the H₂S combustion by the oxygen carrier.
17 It was found that during the reduction of the oxygen carrier (combustion of H₂S)
18 only a small amount of SO₂ appeared in the exit flow from the batch reactor
19 (around 200 vppm); the rest of the sulphur had been absorbed by the oxygen
20 carrier. In the oxygen carrier oxidation only 50 ppm of SO₂ appears in the gas
21 stream exiting from the batch fluidized bed reactor. It can be concluded that the
22 oxygen carrier can “storage” S, that it is slowly released at oxidation conditions.
23 Similar behavior was found by de Diego et al. [38] when natural gas was burnt
24 in a continuous CLC unit with H₂S concentrations higher than 3000 vppm with a

Cu-based oxygen carrier. They found that the oxygen carrier particles reacted with the H_2S and formed Cu_2S or CuSO_4 .

To know which of the oxygen carrier components (metal oxides or support) had more affinity with the sulphur, other TGA experiments were carried out using pure CuO (Panreac, PRS; $d_p < 10 \mu\text{m}$), pure Fe_2O_3 (Panreac, PRS; $d_p < 10 \mu\text{m}$) and MgAl_2O_4 (Baikowski, S30CR). The experiments were done at the same conditions and with the same mixture of reactive gases than the one carried out with the oxygen carrier (3 vol.% O_2 , 8000 ppm SO_2 , 930 °C, 24 h). In the experiments done with MgAl_2O_4 and Fe_2O_3 a increase in the sample weight of 1.5 wt. % was detected in both cases. On the other hand, in the experiment done with CuO , the sample weight increased a 6.6 wt. %, likely due to the reaction of the sample with the SO_2 fed. With these results, it can be said that the oxygen carrier reacts more with the SO_2 than the compounds that form the oxygen carrier particles separately.

In order to determine the presence of sulphur in the particles, used TGA samples were analyzed by SEM-EDX and XRD. Elemental analysis by SEM-EDX, Fig. 6 point 2, showed the presence of Cu, S and O in a stoichiometry corresponding to $(\text{CuO}) \cdot (\text{CuSO}_4)$. The presence of $(\text{CuO}) \cdot (\text{CuSO}_4)$ demonstrated that the increase of weight suffered by the CuO sample was due to the reaction of CuO with the SO_2 , thus being feasible the formation of this compound at temperatures higher than 700°C. However, samples did not show

the formation of any crystalline phase between the sulphur and the Cu, Fe, Al and/or Mg in the subsequent XRD analysis made.

Fig. 6. SEM image of CuO sample used in the TGA (3 vol.% O₂, 8000 ppm SO₂, 930 °C, 24h). Point 1: crystalline CuO; Point 2: amorphous (CuO)·(CuSO₄).

The possible formation of (CuO)·(CuSO₄) in the fuel reactor can affect to the reactivity and/or the oxygen transport capacity of the oxygen carrier. Thus, several samples of oxygen carrier particles were taken from the fuel reactor and analysed by TGA and different solid characterization techniques (XRD, SEM-EDX) to determine if sulphur could be accumulated in the oxygen carrier. Neither, XRD nor SEM-EDX analysis showed any S compound in the oxygen

carrier, although they could be below the detection level. Moreover, the reactivity of used oxygen carrier particles was determined by TGA. Fig. 7 shows the conversion of the decomposition reaction (O_2 release) as a function of time of the fresh and used samples in the CLOU unit. It can be seen that the reactivity was unaffected by operation, although a 10 % decrease in the oxygen uncoupling transport capacity was found, from 4.5% to 4.05%. Assuming that this decrease in the oxygen transport capacity was due to the formation of $CaSO_4$, i.e. 10 mol.% CuO formed $CuSO_4$, it was calculated that a 20% of the total sulphur in coal must be in the oxygen carrier particles. By these reasons, it can be assumed that the partial reaction of SO_2 with CuO present in the oxygen carrier can be responsible of the low S balance closure (see Fig. 4), although did not affect to the oxygen carrier reactivity. It must be also pointed out, that after 35 h of combustion operation at high temperatures and with a high S content fuel, the oxygen carrier did not show any agglomeration problem.

Fig. 7. Conversion vs. time curves for reduction for fresh and after used particles. Reduction in N_2 at 1000 °C in TGA.

3.4. Fate of nitrogen in coal

The nitrogen present in the lignite may be released during devolatilization as NH_3 or HCN. Depending on the combustion conditions, these nitrogenated species can evolve to N_2 , NO, NO_2 or N_2O . In order to carry out a nitrogen balance, N_2 as inert was avoided in all the gas fed to the system. Therefore, CO_2 was used to fluidize both the fuel reactor and the loop seal.

The fate of N in the fuel reactor and air reactor is presented in Figs. 8, 9 and 10 as a function of the fuel reactor temperature. On average, it can be said that 98 wt. % of the nitrogen in lignite was detected in the gaseous phase in fuel and air reactors outlet streams. Fig. 8 shows the splitting of the nitrogen contained in the lignite fed in the experiments at 900, 925 and 945 °C respectively. About 95 wt. % of the nitrogen in coal was found in the fuel reactor outlet and this partition does not seem to be notably affected by temperature.

Fig 8. N distribution during lignite CLOU continuous combustion. : fuel reactor gas outlet; : air reactor gas outlet.

Fig. 9 shows the N-compound distribution of the total N exiting the fuel reactor outlet stream at different temperatures. N_2 and NO were the only compounds detected; thus, NH_3 and HCN generated during lignite devolatilization were oxidized by the oxygen generated by the oxygen carrier particles at the temperatures tested. Then, NO can evolve or not to N_2 , following homogeneous (gas phase) and heterogeneous reactions. Regarding NO_x , only NO was detected and quantified. The analyses showed that NO_2 and N_2O were not formed in the fuel reactor during CLOU combustion. The major nitrogenated specie observed in the fuel reactor was N_2 . According to Fig. 9, around 80 wt.% of the nitrogen evolved in the fuel reactor was in the form of N_2 . During lignite combustion by CLOU process the NO_x formation in the fuel reactor is much higher compared with the NO_x formation in *i*G-CLC process [26]. In *i*G-CLC

process only a 1% of the N that exits from the fuel reactor was as NO_x , however in CLOU process a 20% of the N exist as NO_x . This difference could be due to the presence of free gaseous O_2 in the fuel reactor at CLOU process, which allowed a higher fraction of the N-species as NO, while in iG-CLC process there is a reductive atmosphere that promoted the reduction of NO to N_2 . These results differ from those recently obtained by Song et al. [33] in the CLOU process, burning different solid fuels in a batch fluidized bed reactor with a Cu-based oxygen carrier. They found an important amount of NO_2 together with NO, and N_2O . However in those experiments, unburnt products, such as CH_4 and CO, were detected in the combustion gases, which were not in this work. Moreover, they use N_2 , instead of CO_2 , as fluidizing agent. Both differences can strongly affect to the N fate during the combustion process.

Fig. 10 presents the NO_x emissions measured in the air reactor. In the air reactor, the nitrogen contained in the unconverted char reaching the air reactor was released as a mixture of NO and NO_2 . Total NO_x emissions, as NO_2 , during operation at the different temperatures ranged between 150-180 mg/Nm^3 (6% O_2), lower than the limit set by EU legislation (200 mg/Nm^3 of NO_2 , 6 % O_2). Therefore, the combustion of coal by the CLOU process complies with legislation governing nitrogen-limits.

Fig. 9. Nitrogen compounds distribution measured at the fuel reactor outlet stream at different temperatures

Fig. 10. Nitrogen emissions in the air reactor outlet stream at different fuel reactor temperatures. (---) EU legal emissions.

3.5. Fate of mercury

In coal combustion, the mercury in coal is vaporized when the coal is fed to the boiler. In the test done at 905 °C in the fuel reactor, the mercury species at the outlet of both reactors, fuel and air, were analyzed. Around 13.1 wt. % of the mercury in coal was released from the fuel reactor, while a 15.6 wt. % of the total mercury was emitted in the air reactor. A great part of the mercury fed to the system with the coal, a 42.5 wt. %, was retained as Hg (p). The Hg (p) was detected in two different solid fractions. Part of the Hg fed to the fuel reactor was transferred to the air reactor with the circulating solids (char, ash and oxygen carrier) and eventually could be bounded to the ashes and emitted as Hg (p) (22.5 wt. % of total Hg fed to the system). By the other hand, a 20.0 wt. % was accumulated in the solids bed reactor. The mercury balance closed at 71.2 wt. %, inside the interval proposed as correct (70-130 wt. %) [31, 39].

The mercury concentration emitted from the fuel reactor was 5.5 $\mu\text{g}/\text{Nm}^3$, where the ratio $\text{Hg}^0(\text{g}) / \text{Hg}^{\text{total}}(\text{g})$ was 0.86. Here, Hg^{total} is the total mercury in the gases, i.e. the sum of $\text{Hg}^0(\text{g})$ and $\text{Hg}^{2+}(\text{g})$. This ratio is similar to the one found by de las Obras-Loscertales et al. [40] in a oxy-fuel fluidized bed combustor where $\text{Hg}^0(\text{g}) / \text{Hg}^{\text{total}}(\text{g}) = 0.82$ burning an anthracite at 925 °C. The total mercury exiting in the air reactor gas stream was 1 $\mu\text{g}/\text{Nm}^3$, with a ratio $\text{Hg}^0(\text{g}) / \text{Hg}^{\text{total}}(\text{g})$ of 0.5. Nowadays, there is not legislation about mercury concentration emissions in power systems setup for EU. According with the Directive 2010/75/EU, the maximum mercury emission from incineration systems is 0.05

1 mg/Nm³. Assuming this limit, the concentration emitted from the air reactor was
2 50 times lower.

3 A comparison of these results and the results obtained by Mendiara et al. [26,
4 31] using the same lignite in a combustion unit in the *i*G-CLC process can be
5 made. To compare these values with those obtained in *i*G-CLC mode, they
6 were normalized to a sum of 100 %. Table 4 shows the splitting of gaseous Hg
7 in the fuel and air reactors streams (wt. %). It can be observed that, although
8 the ratios $\text{Hg}^0 \text{ (g)} / \text{Hg}^{\text{total}} \text{ (g)}$ were very similar in both processes for both
9 reactors, the amount of Hg (g) exiting from both reactors was very different. The
10 amount of mercury emitted from both reactors in the case of the CLOU process
11 was 18.6 wt. % and 22.0 wt. % for fuel and air reactors respectively, of the total
12 mercury fed in the coal, in front of a 31.5 wt. % and 67.7 wt. % respectively in
13 *i*G-CLC process [26]. This behavior can be related with the great amount of
14 mercury retained as Hg (p) in the CLOU process in the ashes elutriated from
15 the system, that decrease the mercury gas emissions. These differences
16 between both processes can be explained due to the different reactions that
17 take place and the reaction atmosphere in the fuel reactor in each process. In
18 the CLOU process, the char conversion in the fuel reactor was higher than in
19 the *i*G-CLC process (97% in front of 85%), therefore the amount of mercury
20 volatilized was higher. This volatilized Hg was then more oxidized to Hg^{2+} due
21 to the oxidant atmosphere in the fuel reactor of the CLOU process and the
22 presence of copper in the oxygen carrier. CuO has proved to be more active
23 than Fe_2O_3 for mercury oxidation [41] in experiments on simulated fly ash. As
24 heterogeneous oxidation of mercury on fly ash particles in coal fired boilers is
25 considered as important, or more important, than homogeneous oxidation of

mercury [42, 43] the presence of CuO in the oxygen carrier can enhance heterogeneous oxidation mechanism, both in fuel and air reactors. The high Hg oxidation in the CLOU process could promote its retention in the ashes as Hg (p). Note the low amount of Hg (g) in the fuel reactor exit flow in CLOU (18.6 %) compared to *i*G-CLC (31.5 %).

Table 4. Comparative of mercury fate between CLOU and *i*G-CLC process [26, 31].

iG-CLC		
Splitting (wt.%)	FR = 31.5%	Hg ⁰ 23.6%
	Hg ⁰ (g)/Hg ^{total} (g) = 0.75	Hg ²⁺ 7.9%
	AR = 67.7%	Hg ⁰ 31.1
	Hg ⁰ (g)/Hg ^{total} (g) = 0.46	Hg ²⁺ 36.6
	Hg(p) ≈ 0%	
CLOU		
Splitting (wt.%)	FR = 18.6%	Hg ⁰ 9.6%
	Hg ⁰ (g)/Hg ^{total} (g) = 0.86	Hg ²⁺ 1.6%
	AR = 22.0%	Hg ⁰ 6.6%
	Hg ⁰ (g)/Hg ^{total} (g) = 0.5	Hg ²⁺ 6.6%

	Hg(p) = 59.4%
--	---------------

1

2

3 The Hg (p) retained in the ashes is transferred to the air reactor together with
4 the reduced oxygen carrier and unburnt char. The Hg remaining in the unburnt
5 char was then volatilized in the air reactor and a fraction is oxidized to Hg²⁺.

6 So, this oxygen carrier has the ability to promote the mercury oxidation and the
7 ash particles mostly generated in the fuel reactor could act as a solid within
8 mercury can be accumulated.

9

10 **4 Assessment on pollutant emissions and CO₂ quality**

11 As in any other power generation unit, the emissions to the atmosphere in the
12 air reactor should be under the limits imposed by legislation for different
13 pollutants. Legislation for combustion systems has been set for both SO₂ and
14 NO_x [19], see Table 5. On the other hand, the CO₂ stream from the fuel reactor
15 needs to be compressed, transported and stored. The presence of other
16 components than CO₂ (not only pollutants) in the CO₂ stream is important
17 regarding the CO₂ quality. A guideline about CO₂ quality has been given in
18 Dynamis [24] which must be accomplished to obtain a safety transport and
19 storage. A number of considerations can be drawn from the results obtained in
20 this work. Based on the sulphur, nitrogen and mercury fate, and estimation of
21 the emissions and pollutant concentration in the fuel reactor can be made for a

1 CLOU unit burning the lignite, and a recommendation of the actions to
2 accomplish the legislation limits can be done.

3

4 **Table 5.** SO₂, NO_x and Hg concentrations at the fuel and air reactor outlets in a
5 CLOU unit.

	Depleted Air ¹			CO ₂ Stream		
	SO ₂	NO _x	Hg	SO ₂	NO _x	Hg
	(mg/Nm ³)	(mg/Nm ³)	(mg/Nm ³)	(ppm)	(ppm)	(mg/Nm ³)
Limit	200²	200²	0.05³	100⁴	100⁴	----
CLOU	1300	180	0.001	32000	1800	0.0055
¹ Normalized to 6 vol.% O ₂ ³ Directive 2010/75/EU ² EU legal limit [19] ⁴ Dynamis [24]						

6

7 Regarding SO₂ emissions in the depleted air stream, higher values than the EU
8 legal limits (200 mg/Nm³) would be emitted. These high emissions may be due
9 to both a non-uniform S release during char combustion, resulting from the
10 presence of pyritic S in this coal (2 wt.% in the lignite used) and the oxygen
11 carrier reaction with the SO₂ present in the fuel reactor and it releases in the air
12 reactor, see section 3.3. However, there are two options to decrease the SO₂
13 amount at the air reactor outlet: use an oxygen carrier that does not react with
14 sulphur and install a carbon stripper between the fuel and air reactors. Respect
15 to the first option, it is necessary to continue the development of new oxygen
16 carriers suitable for CLOU process. Regarding the second option, the use of a

carbon stripper decrease the amount of unburnt char transferred to the air reactor, decreasing the SO₂ emissions to the atmosphere. The use of a carbon stripper increases the residence time of the char particles in the fuel reactor, which would allow high oxidation of the pyritic sulphur of the coal. So, the use of a carbon stripper in the CLOU process when a lignite as fuel is used is necessary to decrease the SO₂ emissions to the atmosphere. However, SO₂ emissions in the air reactor higher than EU limit are not expected when typical thermal coals with S contents lower than 1 wt. % and lower pyritic sulphur would be used due to the high char conversion in the fuel reactor obtained by CLOU process [16, 17]. It is expected that most of the sulphur will exit in the fuel reactor exit flow and, therefore, accomplish the EU legislation.

Moreover, as it can be observed in Table 5, an excess of sulphur compounds at the fuel reactor outlet compared to the recommended values were determined. Therefore, systems to reduce the amount of SO₂ in the fuel reactor exit flows must be accomplished. Even with fuels with lower sulphur content, the clean system will be needed. This could be accomplished by wet low temperature absorption using limestone.

Respect to NO_x emissions in the depleted air stream, CLOU process would have lower values than the 200 mg/Nm³ (6 vol. % O₂) limit set by EU legislation [19], see Table 5. Therefore, the combustion of this lignite complies with legislation governing nitrogen-limits in CLOU mode. However, the CO₂ stream leaving the fuel reactor in the CLOU process should be subjected to further

1 treatments in order to reduce the NO_x concentration for safe transport and
2 storage.

3
4 Finally, respect to mercury emissions, the identification and quantification of Hg
5 speciation forms (Hg^0 (g) and Hg^{2+} (g)) done in the present work is relevant due
6 to these mercury species have distinctive chemical, physical and biological
7 properties. Directive 2010/75/EU sets the limits for Hg emissions at
8 incinerations plants to 0.05 mg/Nm^3 (normalized to 10 vol. % O_2 in the outlet
9 stream). The mercury emission measured in the air reactor is 50 times lower of
10 the limit and would not be a problem in a CLOU system, even in case of coals
11 with higher Hg contents. There is not a specification for the maximum amount of
12 mercury in the CO_2 stream; but the risk of corrosion that it can be caused in the
13 aluminium heat exchanges, and the minimization of the undesired reactions, as
14 mineralization and/or precipitation in the CO_2 stream, makes necessary to clean
15 this stream before the CO_2 compression unit to values of concentration less
16 than $0.01 \text{ } \mu\text{g/Nm}^3$, that it is the maximum value allowed by the natural gas
17 processing industry. In case of the fuel reactor outlet stream should be treated
18 to reduce the presence of other impurities, such as SO_2 , and/or NO_x emissions,
19 Hg emissions could be reduced. Combustion systems with SCR, ESP, and wet
20 FGD contribute to increase mercury removal efficiency [39] by removal of Hg^{2+} .
21 Nevertheless, the use of specific systems for Hg^0 (g) removal would be
22 required.

5 Conclusions

The fate of sulphur, nitrogen and mercury was evaluated at different fuel reactor temperatures in the CLOU combustion of lignite in a 1.5 kW_{th} CLOU unit using a novel Cu-based oxygen carrier. The sulphur, nitrogen and mercury compounds present in both fuel and air reactors were analyzed. Complete combustion of CO₂ and H₂O was obtained and high carbon capture efficiency (98.4 % at 945 °C) was achieved. The oxygen carrier particles never showed agglomeration problems. In addition, the oxygen carrier reactivity remained constant.

Regarding sulphur emissions, about 95 wt. % of the sulphur emitted was released in the fuel reactor as SO₂. In the air reactor, SO₂ emissions higher than the legal limit (200 mg/Nm³) were found, which were related to the pyritic sulphur in the ash and/or unconverted char being transferred to the air reactor. The reaction of sulphur with the oxygen carrier, to form (CuO)·(CuSO₄) has been analyzed and confirmed by different characterization studies. The use of a carbon stripper in the system would allow minimizing the SO₂ emissions due to high pyritic sulphur content in this lignite. On the other hand, for typical thermal coals with low S contents, these problems would not be expected.

Regarding the fate of nitrogen in coal, N₂ and NO were the main compounds in the fuel reactor outlet stream, although N₂ was around 80 wt. % of the total nitrogen fed with the coal. In the air reactor, the nitrogen released by the unconverted char was emitted as NO+NO₂, but well below the legislation limit.

Respect to Hg emissions, the total mercury exiting in the air reactor gas stream was $1 \mu\text{g}/\text{Nm}^3$, so the concentration emitted from the air reactor was 50 times lower than the maximum mercury emission from incineration systems at EU legislation, which can be used as reference. However, it will be necessary to clean the fuel reactor stream to reduce the amount of Hg^0 (g) before the CPU unit in order to avoid corrosion problems in the pipelines and in the aluminium heat exchanges.

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NOMENCLATURE

Symbols

F_i	Molar flow of compound i (mol/s)
$f_{\text{C,vol}}$	Mass fraction of carbon in volatiles (-)
f_i	Mass fraction of the element i in coal (%)
M_i	Atomic or molecular weigh of i elements or compound (kg/mol)
$\dot{m}_{\text{coal}}$	Mass-based flow of coal fed-in to the fuel reactor (kg/s)

1	$\dot{m}_{OC}$	Solids circulation rate (kg/s)
2	R_{OC}	Oxygen transport capacity (-)
3	X_{char}	Char conversion (-)
4		
5	Greek symbols	
6	η_{CC}	CO ₂ capture efficiency (%)
7	$\eta_{comb,FR}$	Combustion efficiency (%)
8	ϕ	Oxygen carrier to fuel ratio (-)
9	Ω_{coal}	Stoichiometric oxygen to full combustion of coal (kg O/kg coal)
10		
11	Subscripts	
12	AR	Air Reactor
13	FR	Fuel Reactor
14	outAR	Outlet stream from air reactor
15	outFR	Outlet stream from fuel reactor
16	vol	Volatile matter
17		
18	Acronyms	
19	AR	Air Reactor
20	BET	Brunauer-Emmett-Teller
21	CCS	CO ₂ Capture and Sequestration
22	CLC	Chemical-Looping Combustion
23	CLOU	Chemical-Looping with Oxygen Uncoupling
24	CPU	Compression and Purification Unit
25	CVAAS	Cold Vapour Atomic Absorption Spectroscopy

1	EU	European Union
2	ESP	Electrostatic Precipitators
3	FGD	Flue Gas Desulfurization
4	FR	Fuel Reactor
5	FTIR	Fourier Transform Infrared Spectroscopy
6	GC	Gas Chromatography
7	ID	Inner Diameter
8	<i>i</i> G-CLC	<i>In situ</i> Gasification Chemical-Looping Combustion
9	LHV	Low Heating Value
10	MS	Mass Spectrometry
11	NDIR	Nondispersive Infrared
12	OC	Oxygen Carrier
13	SCR	Selective Catalytic Reduction
14	SEM-EDX	Scanning Electron Microscopy - Energy Dispersive X-ray
15		Spectroscopy
16	TGA	Thermogravimetric analyzer
17	XRD	X-ray diffractometer
18		
19		

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