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Chemical looping combustion in a bed of iron loaded geopolymers

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Abstract

The chemical looping combustion allows for inherent CO_2 separation when burning fossil fuels in presence of a suitable oxygen carrier. The choice of the material to be used should take into account not only chemical/physical properties but also economical, environmental, and safety concerns, addressing for more common materials, like Fe oxides. In this research a geopolymeric oxygen carrier, based on Fe_2O_3, was tested for the first time in a laboratory CLC plant operated at high temperature for the combustion of a CO rich gas from char gasification in CO_2. The CLC plant reliably performed in repeated cycles without decay of the CO conversion during the chemical looping combustion. The maximum CO content in the flue gas was around 1% vol. and carbon monoxide conversion achieved 97%. The calculated oxygen transport capacity was 0.66%. The plant results were confirmed by the XRD analysis that proved the presence of reduced phases in samples after chemical looping stage and by significant peaks obtained during H_2 reduction in TPR equipment.

Keywords: chemical looping combustion; oxygen carrier; geopolymers; hematite; gasification

1. Introduction

The chemical looping combustion (CLC) is a promising two-step combustion method enabling inherent CO_2 sequestration, so that low extra energy is needed for its separation from the rest of flue gases [1]. The process is based on the use of a solid oxygen carrier, usually a metal oxide, which performs the task of transporting the oxygen required for combustion from an air reactor to a fuel reactor, designed as two interconnected fluidized beds [2, 3]. This method, may result more economically advantageous than others (e.g. wet absorption, calcium loop). In this process, indeed, the fuel is introduced to the fuel reactor where it reacts with the oxygen carrier (the metal oxide), at high temperatures, subsequently being reduced to a lower oxidized form [4]. Since both reduction and oxidation

steps may be exothermic, heat can be recovered from both reactors and no large temperature differences can be expected between each other.

Usually the metal oxides chosen to act as oxygen carriers are embedded in a high temperature stable and porous matrix which, eventually, may increase the abrasion resistance of the oxygen carrier itself and improve the oxygen diffusion ability. The extent of the oxidation-reduction reactions involved in the process may vary depending on the reaction conditions and the chemical nature of the adopted metal oxide. Fe, Mn, Ni and Cu oxides have been widely proposed in literature as potential candidates for CLC, in form of pure oxides or in combination [3, 5]. Ni and Cu oxygen carriers have been demonstrated to be very effective, achieving up to 21% of theoretical O transport capacity in the case of NiO reduction to Ni, but they are toxic [6, 7].

Among the different metal oxides that have been proposed so far, iron oxide has a great potential, as it shows relevant advantages, such as the no-toxicity, the large availability, the good resistance to agglomeration and the low-price. Iron oxide can be available in three oxidized forms, FeO (wüstite), Fe_3O_4 (magnetite) and Fe_2O_3 (hematite). It usually behaves by reduction/oxidation of the Fe_2O_3/Fe_3O_4 pair, with a theoretical oxygen carrier capacity equal to 3.34% wt.

In a previous work by the authors [8], a novel oxygen carrier based on iron oxide has been successfully synthesized embedding Fe_2O_3 in a geopolymer matrix. Geopolymers are quasi-amorphous, three-dimensional, and nanostructured ceramic materials that can be produced at low to moderate temperature (25-100 °C) by alkaline activation of alumino-silicate precursors [9] through an easy, low-cost and green process. This class of materials is characterized by a diffused meso-porosity, a rather high surface area, associated with substantially high mechanical strength, abrasion resistance and high temperature stability up to 1000 °C [10-11], properties which make them optimal candidates for fluidized bed operations in CLC systems.

Tests on a granulated metakaolin-based geopolymers added with iron oxide were performed in thermogravimetric equipment and in a lab-scale fixed bed reactor cyclically operated at temperature of 900 °C and atmospheric pressure with a flow rate of reducing and oxidizing gas mixtures (Ar, Ar/CH$_4$) [8]. The Fe_2O_3-doped geopolymer exhibited promising results in terms of higher kinetics, being the geopolymer O carrier more efficient than a commercial Fe oxide in specific operating conditions (short times of reduction and oxidation cycles) and showing higher rate index.

The coal/biomass gasification is a well-developed process for producing a synthetic gas to be converted in further stages. When the gasifying agent is H_2O or CO_2, external heat is required in order to sustain the reactor temperature in the operation range 800-900 °C. If a CLC step is accomplished in sequence to gasification for zero emission combustion, the recirculated hot oxygen carrier can sustain, at least partly, the gasification reactor with benefits for the plant intensification and economics.

The present article reports on a combined gasification-CLC process for the combustion of wood char, with the utilization of an oxygen carrier based on geopolymeric matrix. The results of the experimental tests in a laboratory scale CLC plant and the characterization of the samples from the reactor were presented and discussed in the paper.

2. Experimental

2.1. Experimental equipment

A laboratory scale plant for CLC was used in tests aimed at checking the performance of the oxygen carrier for the conversion of a CO rich gas. As shown in Figure 1, the plant includes two tubular reactors in AISI 316 (22 mm ID and 500 mm length), which are vertically installed inside an electric furnace Carbolite 1200. The first tube (CLC reactor) is filled with alumina wool at both ends and granular oxygen carrier at center (20-30 g), whilst the second tube (gasification reactor) is filled at center with wood char (2-5 g). A system of tubes and control valves (Fig. 1) allows for periodic switching of the operation in the two tubes. A multi-component continuous gas analyzer (mod. GEIT GAS 3160) is used to measure CO, CO_2 and O_2 concentrations in the gas streams from the plant, after the separation of dust and water. A digital manometer monitors the pressure at the base of the gasification reactor. A mass-flow controller (mod. Brooks F21780-001) regulates the flow rate of CO_2 from a bottle, whilst a volumetric pump provides the air for the regeneration.

The plant was initially heated up to the desired temperature in inert atmosphere for the gasification reactor and air for the CLC reactor. Afterwards, three operation modes are feasible by purposely switching the control valves. In a

first operation mode, CO_2 is fed to the gasification reactor and air to the CLC reactor for checking the composition of both gaseous streams exiting the tubes. In a second operation mode, the gas from the gasification tube is fed to the CLC reactor and converted by the oxygen carrier. In a third operation mode, the CO_2 stream is closed and air is fed to the CLC reactor for regeneration. The latter two modes are operated more times in sequence.
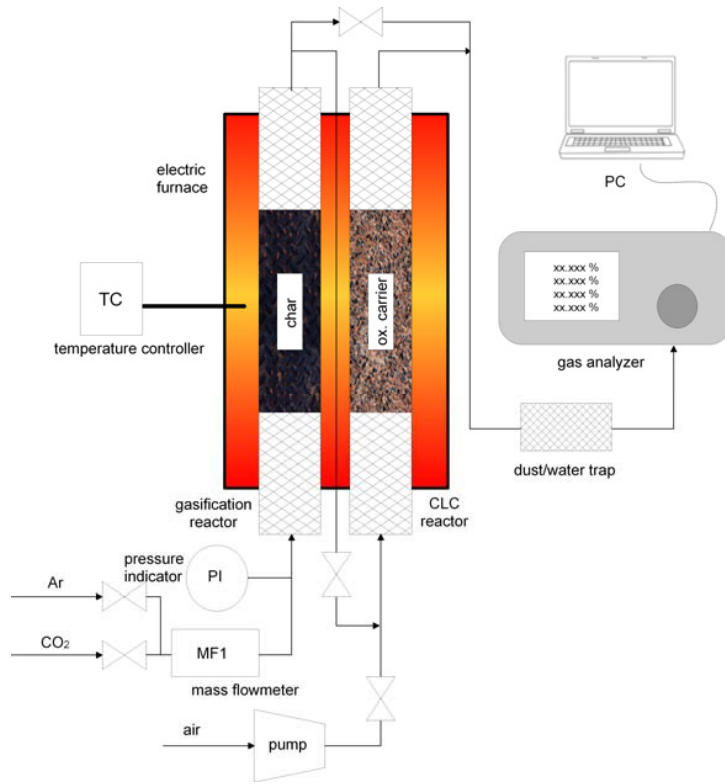

Fig. 1. Schematics of the CLC plant.

The oxygen carrying capacity referred to the mass of the material is calculated by integration over the time of the concentration profiles during CLC and regeneration stages, as reported in Eq. 1 (see Nomenclature for the symbols).

$$C = \frac{Q}{24.02 \cdot W_{OC}} M_W \int (Y_0 - Y) dt \tag{1}$$

A temperature programmed reduction (TPR) characterization was performed using TPD/R/O 1100 analyzer Thermo Quest Company. A thermogravimetric characterization of the oxygen carrier in Ar was carried out up to 900 °C in a Netzsch Geraetebau (STA 449 Jupiter) apparatus. XRD analyses were performed on samples obtained from the experiments in the CLC plant in a Bruker diffractometer (D8 Advance).

2.2. Oxygen carrier material

The geopolymer-based oxygen carrier (GPFe) was prepared by adding a metakaolin powder (Argical M-1200S, IMERYS Minerals, UK) to an aqueous solution of potassium poly-silicate (SiO_2:K_2O=2.0, H_2O/K_2O=13.5), previously obtained by mixing KOH pellets (purity > 99% from Merck) in distilled water and adding fumed silica powder (99.8% from Sigma-Aldrich) under magnetic stirring. The obtained geopolymer slurry had a solid to liquid ratio of 2.3. The mixture was mixed through mechanical stirring for 10 min, then a 325 mesh hematite powder (MRC, Toulouse, France) was added to the slurry to the extent of 51% by weight of dry solid geopolymer reactants. The specific content of iron oxide powder in the mixture was appositely chosen to maximize its percentage in the mixture, and determined by the limit of workability and castability of the paste. The slurries were further mixed for another 10 minutes, placed in sealed silicone moulds and cured at 80°C for 24 h, followed by 24 h curing at room temperature. Finally, the iron-geopolymer monoliths had a Fe_2O_3 content of about 40% wt.; they were roughly crashed in a porcelain mortar and the obtained granules were sieved in the desired grain size fractions of 0.4-0.6 mm.

For TGA tests, Fe_2O_3 powder and geopolymeric GPFe were also mixed with wood char (see paragraph 2.3), fixing the char amount as 7% wt. of the Fe_2O_3 content, according to the stoichiometry 1:1 of the reduction reaction of Fe_2O_3 by C to FeO and CO. The mixture was powdered using an agate mortar to create an intimate contact between C and the oxygen carrier.

2.3. Fuel

Wood char was used as fuel in the gasification reactor. It was produced by fast devolatilization in inert atmosphere at T=750 °C of fir wood and subsequent reduction to the desired size (1-5 mm) by gently crushing and sieving. A thermogravimetric analysis up to T=900 °C of the wood char proved that the residual volatiles content is around 70 % by weight.
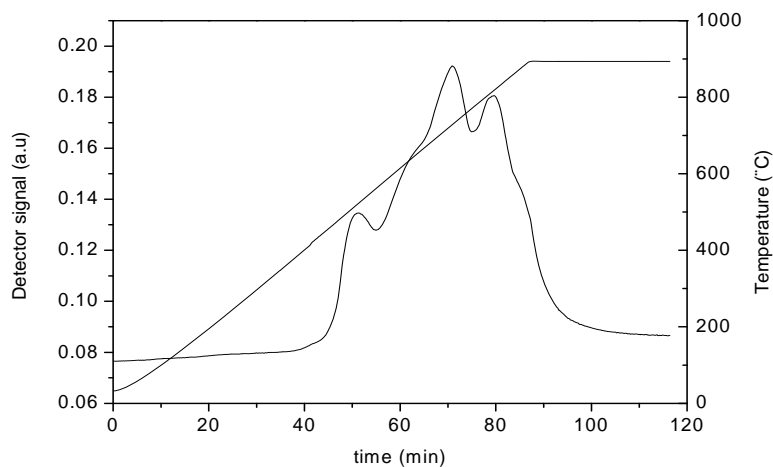
3. Results

Fig. 2. TPR profile for GPFe in H_2/N_2.

Figure 2 shows the result of a TPR characterization of the GPFe oxygen carrier up to 900°C in H_2/N_2 5/95% atmosphere (40 mL/min). Typical peaks are evident for the reduction from hematite (Fe_2O_3) to less oxidized Fe phases. A first peak of reduction is clearly detectable starting at around 400°C that is followed by a main peak located at about 650°C and another peak at 800°C both with shoulders on their side. The spectrum suggests the

occurrence of multiple reductions involving iron oxide phases, possibly altered by the geopolymer binder. Mixed phases, besides pure iron oxides, due to the reaction with the binder were evidenced in the oxygen carrier extracted from the reactor after cycling (see later) and, in addition, a sort of protective action of the binder limiting/retarding the access of the reductive gas can be hypothesized.
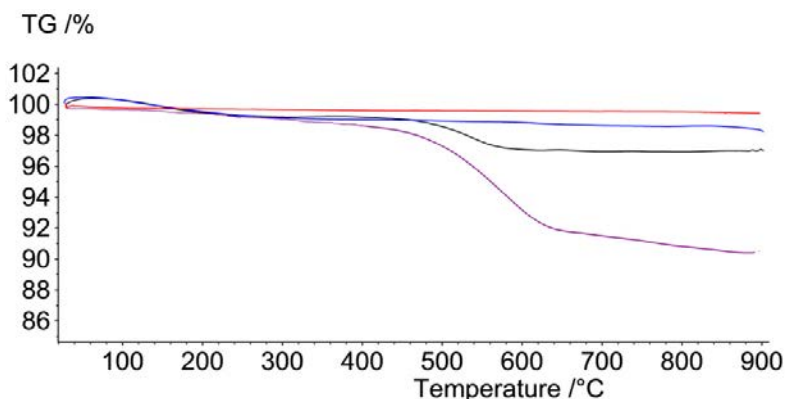

Fig. 3. Loss curves for Fe_2O_3 (red line), GPFe (blu line), Fe_2O_3/char (violet line) and GPFe/char (black line)..

The weight loss curves from TGA experiments are shown in Figure 3 for a series of samples: Fe_2O_3, GPFe, Fe_2O_3/char mixture and GPFe/char mixture. The tests were performed in Ar atmosphere up to 900 °C. The TG curve of Fe_2O_3 keeps a quite constant value up to about 500 °C then a small weight loss of about 0.15 wt% is detected up to 900 °C. GPFe shows an appreciable weight loss up to 300 °C (around 1.2 wt%) that is imputable to the geopolymer fraction and a small weight loss in the temperature range 800-900 °C, similar to the previous sample (Fe_2O_3). This high temperature weight loss could be attributed to a slight O release, even in absence of reducing agents. The behaviors of Fe_2O_3/char and GPFe/char are similar to those of the corresponding carbon-free samples up to around 450 °C. Afterwards, weight losses of about 7.8 wt% and 2.1 wt% are respectively detected in Fe_2O_3/char and GPFe/char up to 900 °C. These values reflect the char content in the mixtures, respectively 7% wt. and 2.7% wt., and are mainly due to the release of residual volatiles from char. Nevertheless, a reaction between the carbon and Fe_2O_3 and direct O exchange probably occurred, in particular in the case of Fe_2O_3/char mixture, where a contact more intimately occurs between fuel and oxidant. In fact, the measured weight loss, i.e. 7.8%, exceeds the value expected from the devolatilization, 4.9% on the basis on a mass balance; the unbalanced weight loss (2.9%) could be attributed to the direct oxygen transport phenomenon. This effect appears more limited in the case of GPFe/char mixture, probably for hindering action of the geopolymeric binder.

The combined results of the TPR and TGA investigations suggest that GPFe oxygen carrier should be preferably employed in a CLC stage in series to a gasification stage, the release of oxygen in inert atmosphere being limited.

Figure 4-a displays two samples of GPFe in the oxidized and reduced state, as obtained from a preliminary test in the CLC plant, where both gasification and CLC stages were accomplished. The typical red color of hematite (Fe_2O_3) was lost after the reduction step performed in the reactor, the particles becoming black in color. The comparison of the XRD spectra (Figure 4-b) confirms that the black color is imputable to magnetite (Fe_3O_4) in the processed sample, where its characteristic peaks clearly appear. The XRD analysis does not highlight presence of the more reduced form FeO, which would be beneficial in order to increase the O transport capacity, and only few residues of hematite were visible. Some hybrid phases of iron-silicates, aluminates or iron-alkali oxides could be also detected, attributable to the high temperature reaction of the geopolymer with the iron species, along with the partial crystallization of some of the amorphous alumino-silicate phases. The complexity of the system and the overlapping of peaks, however, cannot allow identifying the quantitative contribution of each phase in the definition of the pattern. The newly formed crystalline phases, though, did not sensibly affect the final performances of the material, as the ability of GPFe to transport oxygen from air to fuel was confirmed by the test and XRD analysis.
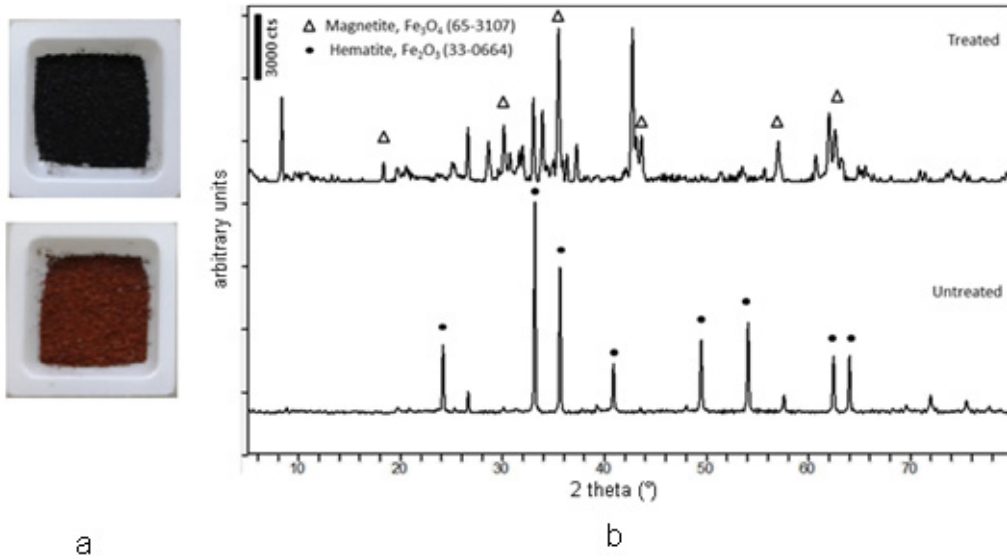
Fig. 4. (a) photographs of GPFe sample before (down) and after (up) a reduction stage; (b) XRD patterns of the sample before (down) and after (up) a reduction stage.

Furthermore, the particle shape and properties were maintained upon the treatment at 900 °C, proving the suitability of the material to undergo repeated cycles of reduction and oxidation.
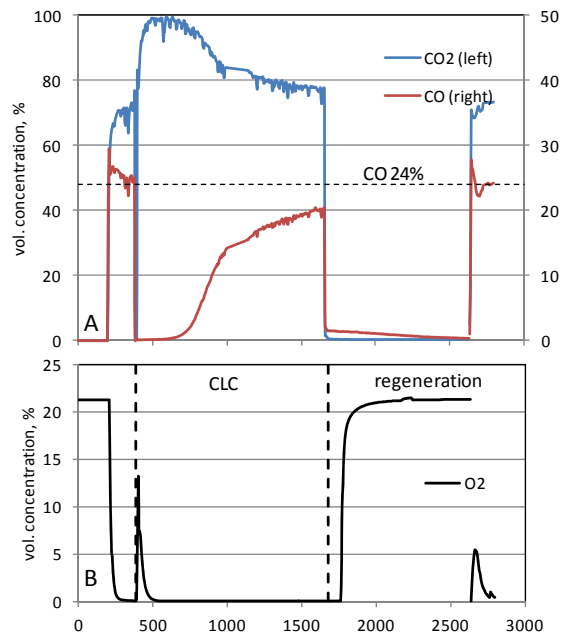

Fig. 5. Concentration profiles of CO_2, CO (A) and O_2 (B) from a single CLC reactor test at 900°C.

Figure 5 displays the concentration profiles along the time for a test performed at 900° C in the CLC plant. In a first stage (t<200 s), the stream exiting the CLC reactor was sent to the analyzer (21% of O_2 in panel B). In a second stage (200<t<400 s), the analyzer was switched to the gasification reactor under flow of CO_2, obtaining a gas with around 24% vol. of CO. In a third stage (400<t<1700 s), the gasification reactor was connected to the CLC reactor and the exiting stream was monitored. In a fourth stage (t>1700 s), air was fed to the CLC reactor for regeneration of the oxygen carrier. Finally (t>2700 s) the composition of the stream from the gasifier was checked, returning again 24% vol. of CO. It is worth noting that during the first stage the air passed without effects throughout the reactor, confirming the oxygen carrier was in the form of full oxidation. During the CLC stage (400<t<1700 s), enhanced conversion of the oxygen carrier occurred as proved by the increase of the CO profile that after t=700 s rises and slowly approaches the limiting value of 24% vol. In the regeneration stage, the O_2 profile presents a breakthrough time of around 100 s, whereas CO and CO_2 promptly decline to zero. This is consequence of the oxidation of Fe_3O_4 to Fe_2O_3, and possible oxidation of deposited carbon. The oxygen carrying capacity, computed via Eq. 1 in the CLC stage, is 0.66%.
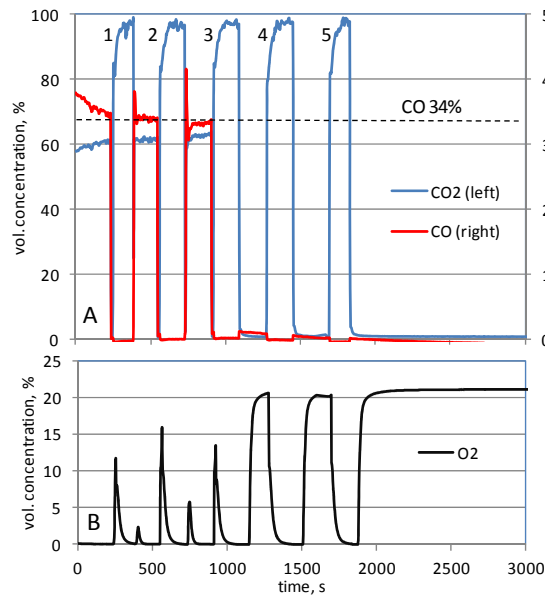

Fig. 6. Concentration profiles of CO_2, CO (A) and O_2 (B) from consecutive CLC reactor tests at T=900°C.

Figure 6 displays the concentration profiles along the time for a test carried out at T=900 °C in the CLC plant with five sequential stages of reduction and oxidation. In the first 2.5 cycles (t<700 s) the analyzer monitored alternatively the gasification unit and CLC reactor, afterwards the composition of the stream exiting the CLC reactor was always monitored. During CLC stage, the CO concentration attains very low values (around 1%) with a conversion efficiency of 97%. The CLC plant reliably operates in repeated cycles without decay of the CO conversion. There is no evidence that the oxygen carrier achieves its maximum value in O transport capacity, thanks to the short operation time of the CLC stage; consequently, it works in more favorable kinetic conditions [8]. Furthermore, the regeneration time (i.e. 3 min.) appears long enough to re-oxidize the oxygen carrier for a further CLC operation.

4. Conclusions

The combined results of the TPR and TGA characterization indicated that the current geopolymeric oxygen carrier should be preferably employed in a CLC stage in series to a gasification stage, although a limited direct interaction between carbon and oxygen carrier was detected.

The geopolymeric oxygen carrier was tested for the first time in a laboratory CLC plant operated at 900°C for the combustion of a CO rich gas from wood char gasification. The CLC plant reliably performed in repeated cycles without appreciable decay of the CO conversion.

The maximum CO content in the flue gas exiting the CLC reactor was around 1% vol. and carbon monoxide conversion achieved 97%. The calculated oxygen transport capacity during CLC stages of 3 min. was 0.66%.

Further developments of the research will focus on the optimization of the oxygen carrier formulation and microstructure, in order to improve its O transport capacity, and the investigation in the CLC reactor of the direct interaction between solid fuel and oxidant.

Acknowledgements

Nomenclature

C	oxygen transport capacity, %
M_w	molecular weight, g mol^{-1}
Q	volumetric flow rate, L h^{-1}
t	time, s
T	temperature, °C
W_{OC}	weight of the oxygen carrier, g
Y	molar fraction, -

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