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Research article

Characterization for disposal of Fe-based oxygen carriers from a CLC unit burning coal

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A B S T R A C T

Chemical Looping Combustion (CLC) is an emerging low cost CO_2 capture technology for large scale power units. The oxygen needed for combustion is supplied by a solid oxygen carrier circulating between two reactors. Fe-based oxygen carriers have been proposed for CLC of coal due to their low cost. Some of them are minerals or industrial residues which can contain toxic trace elements. After its use, the oxygen carrier should be disposed in a landfill and therefore, the presence of soluble toxic elements in the oxygen carrier should be analyzed. In this study, lixiviation tests were carried out with three different Fe-based oxygen carriers used in coal CLC experiments in a continuous unit: ilmenite, a bauxite waste and an iron ore. All the spent oxygen carriers, except the bauxite waste, can be classified as a stable non-reactive hazardous waste and therefore can be disposed in a landfill for non-hazardous residues. An estimation of the amount of solid waste generated in the process based on the fly ash content of the coal and the oxygen carrier particle lifetime was made.

1. Introduction

Among the different CO_2 capture technologies currently under development Chemical Looping Combustion (CLC) is one of the most promising due to the low cost of the CO_2 capture [1]. In CLC, the oxygen needed for combustion is supplied by a solid oxygen carrier. In most of the cases, the oxygen carrier is a metal oxide (based on Ni, Cu, Fe, Mn or Co), represented by M_xO_y, which is continuously circulating between fuel and air reactors as shown in Fig. 1.

One of the aspects that should be taken into account in a further scale up of this technology is the possible generation of solid residues from the CLC unit due to oxygen carrier losses. On the one hand, the oxygen carrier may suffer attrition and therefore be lost by elutriation (F_1 and F_2 in Fig. 1). The elutriated material would be recovered to avoid emissions of particulate matter to the atmosphere or damage to the equipment placed downstream. On the other hand, when a solid fuel (especially coal) is burned, it may be necessary to eliminate ashes from the CLC system to avoid accumulation in the reactors leading to operational problems. In principle, ashes can be separated from the oxygen carrier on the basis of density and particle size differences. Nevertheless, in the drainage of the ashes, some oxygen carrier particles may be lost despite the efficiency of the separation system used [2]. This is represented by F_3 in Fig. 1. Therefore, to maintain a constant inventory in the CLC system a makeup flow of new material should be fed (F_0) and the used particles that were recovered should be characterized in order to be disposed.

The proper management of the used oxygen carriers in a CLC process is an important issue due to the magnitude of the waste stream that could be generated and the possible toxicity of some of the metals that compose the oxygen carriers. Nevertheless, few studies have addressed this aspect of the CLC technology to date. Some of them have been mostly focused on the evaluation of the cost for the makeup flow that should be fed to the CLC unit [3]. In our previous work by García-Labiano et al. [4], we considered several aspects related to recovery, recycling and landfilling of an oxygen carrier. The study was focused on a copper-based oxygen carrier used in a CLC unit burning gaseous fuels.

In case of CLC for coal as fuel, low cost materials based on Fe-based minerals and industrial residues have been used in continuous CLC units [5–12]. All of them are cheap materials and therefore the recycling or recovery process for the used oxygen carriers is not an interesting option from an economic perspective. However, disposal of these spent oxygen carriers should be considered, even more in the case of industrial residues as they may contain important quantities of heavy metals. Heavy metals can represent a concern for human health, especially the exposure to Pb, Cd, Hg and As, although other metals like Cr, Cu, Mo, Ni, Sb, Se, Sn, V and Zn are also usually controlled by environmental rules and regulations. Leaching tests are frequently used to characterize the potential of a solid waste to leach when disposed in a landfill. The current European regulation regarding the leaching properties of waste materials is covered by the Council directive 1999/31/EC and the Council decision 2003/33/EC. They determine the criteria required to dispose waste in landfills and classify the waste materials into one of the three categories: hazardous, non-hazardous and inert waste.

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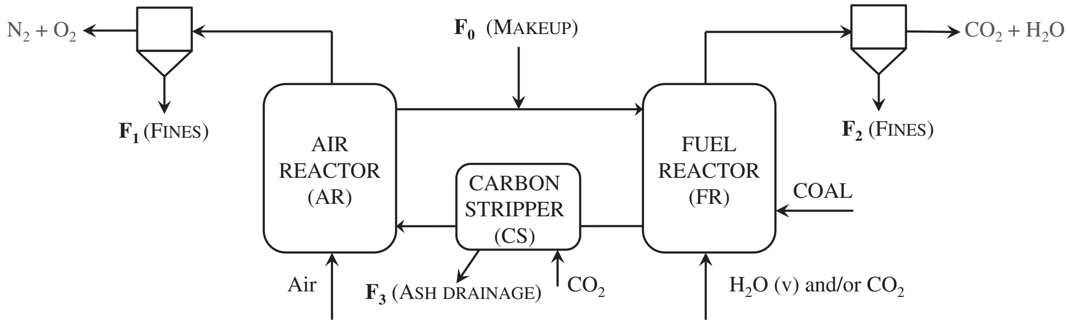

Fig. 1. Schematic diagram of a CLC process burning coal. F_i represent solids streams in the system.

The present work is centered on the characterization for disposal of different Fe-based oxygen carriers used in a CLC unit. The leaching properties of three of the most recently used oxygen carriers in CLC units burning coal are evaluated: ilmenite, a bauxite waste and an iron ore. All these oxygen carriers were tested for coal combustion in a continuous 500 W_{th} CLC unit at the Instituto de Carboquimica (ICB-CSIC-s1) [6–8]. Leaching tests according to the CEN 12457–3 standard will be conducted to characterize these residues and to evaluate the possibilities of disposal for these materials. Moreover, a global mass balance of the CLC process for coal considering the oxygen carrier lifetime and the oxygen carrier lost with the ashes will be also carried out in order to have an estimation of the amount of solid waste generated in the process.

2. Material and methods

2.1. Materials used

This study was focused on the three oxygen carriers previously used in CLC coal combustion experiments in the ICB-CSIC-s1 unit at Instituto of Carboquimica: ilmenite (ILM) [6,9–11], a bauxite residue, named as iron-enriched sand fraction (Fe-ESF) [7,12] and an iron ore (Fe-ore) [8]. In all the experiments, a bituminous Colombian coal "El Cerrejón" was used as fuel (+200–300 μm). Ultimate and proximate analyses of this coal are shown in Table 1. The particle size for all the oxygen carriers used in the experiments was +100–300 μm. A full description of the unit and the experiments can be found in references [6–12].

Fine particles produced by attrition in the reactors are not collected by the cyclone and they escape from the unit. These particles were collected in filters at the fuel and air reactor outlet. Recovered particles mainly consisted of elutriated oxygen carrier particles and fly ash. Only the particles with a size lower than 40 μm were considered as fines. Fig. 2 shows a typical particle size distribution and the corresponding cumulative curve for the fines collected. They were determined by a laser diffraction particle size analyzer LS 13320 Beckman Coulter. According to Fig. 2, around 90% of the particles collected are below 40 μm. These particles, denoted as "fines", cannot be re-used in the CLC facility and they are representative of particles in F_1 and F_2 streams in Fig. 1. Due to the reduced dimensions of the CLC unit, no system for bottom ash separation was included in this setup. Nevertheless, ash particles were not accumulated in the CLC unit because most of them were recovered as fly ash in the filters. Although ash particles were not accumulated in this unit, coarse particles from the air reactor were also collected as representative oxygen carrier particles in the purge stream F_3 in Fig. 1.

Table 1
Ultimate and proximate analysis of the bituminous Colombian coal used [6].

Proximate analysis (wt.%)	
Moisture	2.3
Ash	8.8
Volatile matter	33.0
Fixed carbon	55.9
Ultimate analysis (wt.%)	
Carbon	65.8
Hydrogen	3.3
Nitrogen	1.6
Sulfur	0.6
Oxygen	17.6
LHV (kJ/kg)	21,900

Ilmenite is a mineral widely used in CLC with solid fuels [5]. The ilmenite used was extracted from a Norwegian natural ore. Before being used in the experiments in a continuous unit, the sample was calcined in air at 950 °C during 24 h to ensure complete oxidation. Calcined ilmenite consists of a mixture of Fe_2TiO_5, Fe_2O_3 and TiO_2. Solid samples characterized in this work were extracted from the combustion experiments at the ICB-CSIC-s1 unit, where a total of 42 h of continuous operation was registered [11].

Due to its reactivity and low cost, the stabilized iron enriched sand fraction of a solid bauxite residue (Fe-ESF) has been used in recent works as oxygen carrier for CLC of coal [7,12]. After bauxite digestion in the Bayer process, the Fe-enriched residue is generated and it mainly consists of Fe_2O_3 and Al_2O_3. Fe-ESF may contain different heavy elements such as Cr or V [13]. The Fe-ESF received was calcined at 1200 °C during 18 h to stabilize the material and increase the mechanical strength. The total content of Fe_2O_3 in the sample used in the experiments at ICB-CSIC-s1 was 58%. It was used during 55 h of continuous operation [7].

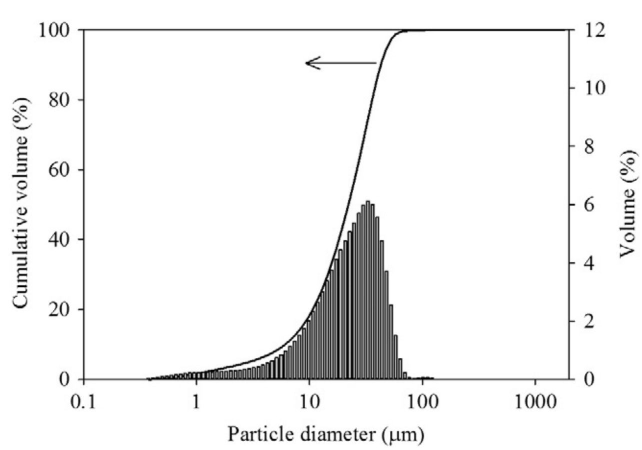

Fig. 2. Particle size distribution of the fines collected in CLC of coal with Fe-ESF as oxygen carrier.