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

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Abstract

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.

Keywords: combustion, coal, CO_2 capture, chemical looping, iron oxygen carries, disposal

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 Figure 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 Figure 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 Figure 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 content 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, 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 three categories: hazardous, non-hazardous and inert waste.

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. Figure 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 Figure 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 Figure 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 Figure 1.

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 950ºC during 24 hours 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 hours of continuous operation were 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 1200ºC 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 hours of continuous operation [7].

An iron ore denoted as Tierga iron ore (Fe-ore) showed higher reactivity than both ilmenite and Fe-ESF in coal CLC and was recently studied for CLC of solid fuels [8]. Prior to its use, the iron ore was calcined at 950ºC during 12 hours in order to increase the mechanical strength. In addition, the dolomite also contained in the sample decomposes during the calcination process to CaO and MgO, which were mainly lost as fines during the first hours of operation in the CLC unit [8]. The Fe_2O_3 content of the Fe-ore used at ICB-CSIC-s1 once calcined was 76.5%. The Fe-ore ore was used during 50 hours of continuous operation.

Table 2 summarizes the composition (wt.%) of ilmenite, Fe-ESF and Fe-ore for the different solid streams in the continuous CLC unit determined by inductively coupled plasma (ICP-AES) using a Jobin Ybon 2000 apparatus. These solids are calcined particles, fine particles in filters downstream the cyclone and particles from the fluidized bed. They can be considered as representative of makeup particles (F_0), elutriated particles (F_1+ F_2) and coarse particles mixed with ash (F_3), respectively. Morevoer, the composition of the coal ashes is also shown in Table 2. For that purpose, ashes from the bituminous coal were prepared in a muffle. The coal was heated in air at 5 ºC/min up to 815ºC. This temperature was maintained for at least 1 hour to ensure complete combustion of the coal and then the sample was cooled down. The composition was also determined by ICP-AES.

2.2 Experimental setup and procedure

The used oxygen carriers should be classified as hazardous, non-hazardous or inert residues in order to be correctly disposed. The criteria and procedures required for the admission of the different residues in landfills are set by the Council decision 2003/33/EC. Apart from the basic characterization of the corresponding residue, these procedures include leaching tests. According to the Council decision 2003/33/EC decision, the presence of several metals in the eluate obtained from the oxygen carrier samples should be checked in order to classify these residues. In the case of the oxygen carriers being considered in this study and according to the above legislation, the metals in Table 2 whose concentration in the eluate represent a potential risk and therefore should be measured are Cd, Cr, Ni, Pb and Zn. Excessive quantity of these metals are deadly poisonous to human an aquatic organisms. Arsenic metal content in the different samples was also determined but never detected, therefore the analysis of this metal in the eluates was not carried out.

There are several types of leaching tests to evaluate the solubility of the constituents of a solid material. Laboratory tests fall into two general categories: single extraction/batch tests and multiple extraction/flow-around and flow-through leaching test. The latter are normally used when information about the kinetics of contaminant mobilization is needed. In this work, a single extraction batch test was considered appropriate to analyze the oxygen carriers before and after operation in the CLC unit, as well as the fines recovered during operation. Leaching tests were carried out following the methodology described by the standard CEN 12457-3. The same standard test was used in leaching tests of oxygen carrier materials previously reported [4]. CEN 12457-3 is a two-stage batch leaching test performed at a cumulative liquid to solid (L/S) ratio of 10 L/kg (first leaching test step, 6 hours at L/S = 2; second step, 18 hours at L/S = 8 L/kg). This test is intended for materials with high solid content and with particle size below 4 mm. Leaching tests were carried out by duplicate and it was assumed that equilibrium or near equilibrium was achieved between the liquid and solid phases during the test period. Reaching equilibrium in single extraction leach testing is critical to predicting leaching behaviour over long periods of time. This two-stage leaching test is expected to reproduce more closely the field conditions since these include successive leaching stages at low L/S ratios, rather than a single stage at a high L/S ratio. After each leaching step, the residue which was not dissolved was separated by filtration using a membrane filter of 0.45 µm prewashed with distilled water.

The leaching tests were performed at ambient temperature. Around 12.5 g of the corresponding oxygen carrier were introduced in a polypropylene bottle and mixed with distilled water (25 mL at L/S=2; 100 mL at L/S=8). The bottles were placed in an agitated rotating device ROTAX 6.8 from VELP Scientifica. The rotation velocity was set to 10 rpm as established by the standard. The value of pH in the eluate was recorded and the metal concentration determined by ICP-AES for each L/S fraction. The pH measurements were done immediately after the eluate was filtrated with a portable pHmeter from XS Instruments PH7X. The proposed limit values (PLV) for Cd, Cr, Ni, Pb and Zn in the eluates according to the European Council Decision 2003/33/EC are summarized in Table 3. Leaching tests were carried out to particles susceptible to be considered for disposal, i.e. fines (F_1+F_2) and coarse particles (F_3) from material used in the CLC unit. In the case of the Fe-ESF sample, lixiviation tests were also performed to the calcined material due to the high Cr content. As it was previously mentioned, the objective of this work was to evaluate the lixiviation behaviour of the different Fe-based oxygen carriers. Nevertheless, lixiviation test of the ashes from the bituminous coal were also carried out in order to estimate the contribution of the ashes to the lixiviation of the fines recovered from the continuous unit, as the ashes will be mixed with the oxygen carrier in some proportion.

3. Results and Discussion

3.1 Lixiviation tests

As mentioned before, lixiviation tests were carried out with two samples: (1) solids in the air reactor bed; and (2) fines collected in the filters. In the ICB-CSIC-s1 unit and due to its design and the coal used (bituminous Colombian), bed samples contained negligible amount of ashes. Most of the ashes appeared as fly ashes together with the fines collected in the filters. A rough estimation of the fraction of ashes in solids recovered in the filters can be done by determining the iron content in the fines, the amount of iron in the calcined oxygen carrier (F_0) and the composition of the ashes in the bituminous Colombian coal (included in Table 2). Thus, ash fraction in fines was estimated as 4.4% for experiments with ilmenite, 1.8% for experiments with Fe-ESF and 14.8% for experiments with the iron ore.

Table 3 presents the values (in mg/kg dry matter) obtained in the lixiviation of bed samples and fines obtained for the three Fe-based oxygen carriers, together with the average pH value of the eluates in each case. These values can be compared with the PLV values also included in this Table. Results for the lixiviation of the coal ashes were also included in Table 3.

3.1.1 Ilmenite (ILM)

In the case of ilmenite (ILM), the fractions of Cd, Cr, Ni, Pb and Zn in the dried sample obtained in the eluates of the solids extracted from the bed sample (F_3) are below the PLV values for the two L/S ratios considered in the standard. The average pH values obtained after lixiviation at L/S = 2 and L/S = 10 were 9.4. The lixiviation of the fines revealed higher values of chromium in the eluates when compared to the coarse material, although they are below the PLV and therefore this should not represent a problem to dispose ilmenite fines in the landfill. The value of the average pH was 7 in the case of the eluates from ilmenite fines. Both, coarse and fine ilmenite particles are classified as stable non-reactive hazardous wastes.

3.1.2 Tierga iron ore (Fe-ore)

The results for the Tierga iron ore (Fe-ore) show similar conclusions to ilmenite. The PLV values for Cd, Cr, Ni, Pb and Zn are by far not exceeded and the average pH value is 11.7 in the case of the samples from the bed. Similar conclusions can be obtained in the leaching of the iron ore fines. Therefore, Fe-ore can be classified as stable non-reactive hazardous waste.

3.1.3 Bauxite waste (Fe-ESF)

For the case of the bauxite waste (Fe-ESF), the presence of chromium in the eluates is more significant compared to the rest of the metals. This could be expected, as the amount of this metal showed in Table 2 for the different streams of bauxite waste was already the highest of the three oxygen carriers. Chromium is an especially toxic metal which can cause severe environmental and human health problems. Therefore, the behaviour of this oxygen carrier was more deeply studied compared to ilmenite and the iron ore.

Prior to use this material as an oxygen carrier in the CLC unit, it was calcined during 18 hours at 1200ºC in order to increase the mechanical strength and stabilize the residue. In order to check the effect of the calcination in the stabilization of this material, lixiviation tests were carried out to the sample after calcination. Table 3 show the results obtained for Cd, Cr, Ni, Pb and Zn in the eluates. For the two L/S ratios tested, the values obtained for the metals analyzed in the eluates were below the PLV values except for the case of chromium, where the limit was clearly exceeded. Nevertheless, the concentrations found for Ni, Pb and Zn were very low, even negligible in some cases.

Results indicate that the chromium contained in the Fe-ESF calcined sample was easily liberated. Chromium in the bauxite residue is present as Cr^{3+} substituted into hematite [14]. It is known that Cr^{3+} is sparingly mobile, due to its low solubility, high adsorption and complexation. This is not the case [15] of the more oxidized state Cr^{6+}, which in addition is highly toxic and a potential risk for human health. Following the results in Table 3, it can be deduced that Cr^{3+} in the Fe-ESF sample was converted in some extent to Cr^{6+} during calcination at 1200ºC in air and therefore chromium was released in the eluate. The oxidation of Cr^{3+} to Cr^{6+} at high temperatures has been reported before in literature [16, 17]. Actually, according to different authors, the oxidation of Cr^{3+} to Cr^{6+} can take place under the presence of oxygen and manganese dioxide [18-21]. According to the composition of the Fe-ESF calcined sample presented in Table 2 and the amount of chromium recovered in the eluate, the extent of Cr^{3+} oxidation to Cr^{6+} can be estimated as 1%. Although the calcination increased the mechanical strength of the Fe-ESF residue, it was not beneficial from the chromium stabilization point of view.

As mentioned before, the calcined Fe-ESF sample was introduced in the continuous CLC unit and 55 hours of continuous combustion were performed. After the combustion experiments, lixiviation tests were conducted to samples from the air reactor bed and to fines recovered in the filters at the outlet of fuel and air reactors.

Results of the lixiviation tests performed with the bed material and the fines are shown and compared in Figure 3. Only results corresponding to Cd and Cr are represented because of the important presence of chromium in the oxygen carrier and in the case of cadmium, because it is the element with the lowest PLV. The amount of Cd and Cr per kilogram of dry sample was lower than the corresponding PLV values for the two different L/S ratios, except for the case of Cr in the Fe-ESF fines when L/S =2 ratio was used. The average pH observed in the lixiviation of the bed samples was 11.0 and in the case of the fines 11.2. Several interesting conclusions can be drawn from the results shown in Figure 3. First, the influence of the particle size in the leachability of the Fe-ESF oxygen carrier. The values of chromium found in the eluates from the fine particles were around 3.5 times those encountered in the lixiviation of the bed samples. This fact would confirm observations made in previous studies about the small size of the fines that could affect the leachability of some metals, favouring it [22, 23]. The other fact is that the values obtained for chromium after several operating hours in the CLC unit at high temperatures were not larger than those observed for the calcined sample in Table 3, revealing that the extent of Cr^{3+} oxidation to Cr^{6+} did not increase with the time at high temperatures. It has been observed that Cr^{3+} oxidation to Cr^{6+} could be reversed in the presence of some electron donors such as organic matter and Fe^{2+} compounds [24, 25]. During the reduction reactions in the fuel reactor of the CLC unit, the presence of reducing compounds, e.g H_2, CO and CH_4, can reduce the Cr^{6+} present in the Fe-ESF oxygen carrier, forming Cr^{3+} whose leachability is much lower. The possible contribution of coal ashes to the Cr presence in the eluates of the Fe-ESF samples can be also considered small, first due to the low percentage of ashes in the Fe-ESF samples and second due to the low Cr concentration found in the eluates from the ashes, shown in Table 3.

Nevertheless, although the Cr lixiviation of the used Fe-ESF was not as favoured as in the original calcined sample, the residues (especially fines) obtained in the continuous unit exceed the limits established by Council decision 2003/33/EC to be considered as non-hazardous waste. Following the lixiviation values obtained in the text, the used Fe-ESF could be disposed in a landfill for hazardous materials. For this purpose, the above legislation set lixiviation limits of 25 mg Cr/kg dry for L/S=2 and 70 mg Cr/kg dry for L/S=10.

Despite the high content of Cr in the eluates of the used Fe-ESF samples, it is interesting to highlight that, compared to the results obtained with the calcined material, these values of Cr in the eluates are lower and therefore, the use of Fe-ESF in the CLC unit contributes to stabilize the potential toxicity of this residue. Pre-treatment before being disposed in a landfill could be another option to handle used Fe-ESF. During the years, different methods for heavy metal removal and/or stabilization in residues have been proposed [26, 27].

3.2 Estimation of the residues generated in a continuous CLC unit

According to the results previously presented, two of the three low-cost oxygen carriers tested could be disposed in a landfill for non-reactive hazardous wastes. Nevertheless, besides toxicity, another aspect that would be interesting to evaluate is the amount of residues that can be generated per year in a normal operation of a CLC plant. This evaluation could facilitate the comparison with the current combustion technologies, such as pulverized coal combustion.

In order to evaluate the amount or residues generated, some assumptions were made. Calculations were performed considering 1 MW_{th} of coal. From previous studies on CLC combustion using coal [28], it was estimated that an optimum amount of oxygen carrier in the fuel reactor to reach acceptable combustion efficiency values was 1000 kg/MW_{th}. Then, considering the solids in the air reactor, the total solids inventory in the system would be around 2000 kg/MW_{th}. The bituminous Colombian coal used in the experiments in the continuous ICB-CSIC-s1 unit was taken as reference (see ultimate and proximate analysis in Table 1). It was estimated that this corresponds to a coal feed of approximately 0.046 kg/s.

On the other hand, the two possible oxygen carrier losses in the 1 MW_{th} coal CLC unit would be the fines recovered by filters at the outlet of fuel and air reactors and the material that may be lost in the drainage of the bottom ashes. In the operation in a 1 MW_{th} unit it is expected that the oxygen carrier lost in the drainage of the ashes would content a larger fraction of resistant ashes compared to the 500 W_{th} unit, where most of the ashes were lost as fly ashes.

The oxygen carrier lost as fines ($\dot{m}_{fines}$) could be estimated from the attrition rate values ($r_{attrition}$) previously observed in the experiments in the ICB-CSIC-s1 continuous unit with the three oxygen carriers. This attrition rate was calculated experimentally as the mass percentage of particles with a size smaller than 40 µm lost per hour of operation. The corresponding values were 0.076 % / h in the case of ilmenite [6], 0.2 % / h in the case of Fe-ESF [7], and 0.1 % / h for the iron ore [8].

$$\dot{m}_{fines} = m_{OC} \cdot r_{attrition} \tag{1}$$

where m_{oc} is the total solids inventory in the system. In all the calculations, it was estimated that the 1 MW_{th} CLC unit operated during 8000 h per year. Considering this, the oxygen carrier lost as fines would be 12 t/year for ilmenite, 32 t/year for Fe-ESF and 16 t/year for Fe-ore, in all cases per MW_{th}.

The oxygen carrier lost in the drainage of the ashes ($\dot{m}_{OC,drain}$) may depend on the efficiency of the separation system used and on the ash content of the coal. In the calculations presented, two types of ashes are considered: fly ash and resistant ash. Only resistant ashes can be accumulated in the CLC system and should therefore be drained. This ash percentage in the fuel reactor (f_{ash}) was set as 50%. A higher fraction of ash compromises the oxygen transport capability from the air reactor. A lower value would result in a high replacement rate of the oxygen carrier in the system [29]. Under these conditions, the calculation of the oxygen carrier lost in the drainage of the ashes ($\dot{m}_{OC,drain}$) can be done as follows:

$$\dot{m}_{OC,drain} = \frac{1 - f_{ash}}{f_{ash}} \cdot \dot{m}_{ash} \cdot (1 - f_{fly,ash}) \tag{2}$$

where $f_{fly,ash}$ represents the fraction of fly ashes in the coal used and $\dot{m}_{ash}$ is the total ash flow being introduced to the 1 MW_{th} CLC system. The sum of the two oxygen carrier flows calculated with equations (1) and (2) represents the total makeup flow that should be introduced in the CLC system to maintain the total solids inventory.

The oxygen carrier in the fines will be mixed with certain amount of fly ashes. In case that the fraction of fly ashes in the coal is high, it would be especially interesting that the attrition rate is low to minimize the amount of residues generated. On the other hand, the oxygen carrier drained from the fuel reactor will also contain up to 50% resistant ashes. Both streams are the residue streams generated in the CLC unit. Considering all this, Figure 4(A) shows the estimations for the total residues generated per year and MW_{th} using as a variable the percentage of fly ashes formed from coal ash. If no fly ashes are generated, then the amount of solid residues produced would be 240 $t/year·MW_{th}$ for ilmenite, 263 $t/year·MW_{th}$ for Fe-ESF and 247 $t/year·MW_{th}$ for Fe-ore. Otherwise, if all the ashes from coal were fly ashes, the total amount of residues generated would correspond to the sum of the losses in attrition (12 t/year for ilmenite, 32 t/year for Fe-ESF and 16 t/year for Fe-ore) and the ashes generated from this bituminous coal (115 t/year). These values can be compared to general figures for these materials in the literature. In the case of the Fe-ESF material, the annual production of the raw residue is around 55-65 %wt. of the bauxite processed, which represented around 75 Mt [30].

Finally, Figure 4(B) analyzes the composition of the solids recovered in the filter at the outlet of the reactors. Figure 4 (B) shows the percentage of oxygen carrier in these fines depending on the amount of fly ashes in the coal. As it could be expected, the percentage decreases when the percentage of fly ash is higher. If all the ashes in coal were fly ashes, then the percentage of oxygen carrier in the fines would be quite low (9.5% for ilmenite, 21.7% for

Fe-ESF and 12.1% for Fe-ore). The highest percentage of oxygen carrier in the fines will always correspond to the material with the highest attrition rate, in this case Fe-ESF.

One of the first approaches to reduce the residues generated in a CLC unit would be the improvement of ash separation in the drained stream from the fuel reactor in order to minimize the amount of oxygen carrier lost in that stream. The design of the fuel reactor in the CLC system would have also an impact on the amount of residues generated. The configuration/size of the fuel reactor would modify the maximum amount of ashes allowed in the bed to make operation feasible. Another aspect influencing the amount of residues produced is the type of coal being burned. Coals with high ash content would increment the residues produced per year. Moreover, the evaluation of the nature and amount of solid residues generated presented above can help to design reutilization approaches for these residues. In the case that the coal used in the CLC unit presents a high fraction of fly ash, then the solids recovered after the filters (fines) can be considered as mainly coal ashes and then be used in the same reutilization processes as the ashes currently produced in power generation units (concrete, low cost adsorbents, mine back fill, road sub-base, etc). If the coal fly ash fraction is low, the fines recovered in the filters can be treated as mainly oxygen carrier and they could be used in similar applications as they were used originally. In the case of the materials used in these work, ilmenite can be reused in the production of titanium and the Fe-ore can be reused in the production of pigments. For intermediate cases, when the amount of ash and oxygen carrier is similar, the residues generated should be disposed in a landfill with prior evaluation of their potential lixiviation characteristics. As it was previously mentioned, ilmenite and the Fe-ore are not expected to generate landfilling problems, as they can be disposed in a landfill for non-reactive hazardous wastes. In the case of the Fe-ESF material, this would not be possible, but it is a significant advantage that the use of this bauxite waste in the CLC system has contributed to stabilize this waste when compared to its original state.

As it was mentioned before, Chemical Looping Combustion (CLC) is one of the most promising carbon capture technologies due to the low cost of the CO_2 capture associated to it. The cost of the fresh oxygen carrier added to the CLC unit represents the main operational cost per ton of CO_2 avoided in a CLC process [3]. This cost is related to the makeup flow. Considering the previous results, an estimation of the cost per ton of CO_2 avoided in the CLC process has been made. The cost of the makeup flow of oxygen carrier per ton of CO_2 avoided, $\chi_{OC,}$ was calculated as [3]:

$$\chi_{OC} = 10^3 \cdot \dot{\mu}_{0,OC} \cdot C_{OC} \qquad (3)$$

where $\dot{\mu}_{0,OC}$ is the flow of new oxygen carrier added (kg/s) per kg/s of CO_2 avoided and C_{OC} is the unit cost of solid oxygen carrier (€/kg OC). When solid fuels are considered, the total makeup flow to be introduced in the CLC system is the sum of the two oxygen carrier flows calculated with equations (1) and (2). Thus equation (3) can be rewritten as:

$$\chi_{OC} = \left[(\dot{m}_{fines} + \dot{m}_{OC,drain}) \cdot \frac{LHV}{s_e} \right] \cdot C_{OC} \qquad (4)$$

where LHV is the low heating value of the solid fuel used (MJ/kg), s_e is the specific emission defined in this case as the kg of CO_2 produced per kg of solid fuel.

The value of s_e can be determined using the elemental composition of the bituminous Colombian coal presented in Table 1. The unit cost of the Fe-based oxygen carriers was estimated as 0.15-0.2 €/kg for ilmenite and 0.1-0.15 €/kg for the Fe-ore [31]. In the case of the Fe-ESF material, the unit cost was more difficult to be estimated, because it is a residue and therefore available at no cost. However, a unit cost of 0.02 €/kg was assumed considering the cost derived from the calcination of the material. It has been observed that the Fe-ESF residue should be calcined at high temperature for its stabilization prior to be used [32].To estimate the calcination costs, it was assumed that the energy required for the calcination of Fe-ESF would be similar to the energy consumed in a rotary kiln used in clinker production (3.35 MJ per kilogram of product) [33]. It was also assumed that this energy was supplied by natural gas combustion. The cost for Fe-ESF calcination was estimated considering that the price for natural gas was 0.023 €/kW·h.

Figure 4(C) summarizes the results obtained for the oxygen carriers studied in this work considering a 1 MW_{th} continuous CLC unit burning coal. For ilmenite and the Fe-ore two lines appear in Figure 4(C), corresponding to the maximum and minimum value of the cost estimated for the oxygen carrier. As it can be seen in Figure 4(C), the cost of the makeup flow per ton of CO_2 will depend on the percentage of the fly ashes in the coal being burned. The amount of fly ashes will affect the amount of oxygen carrier lost in the drainage of the resistant ashes in the fuel reactor, which will decrease as the percentage of fly ashes increases. If all the ashes were fly ashes, the cost per ton of CO_2 would correspond to the oxygen carrier lost by attrition (0.6-0.8 €/ton CO_2 for ilmenite, 0.2 €/ton CO_2 for Fe-ESF and 0.5-0.8 €/ton CO_2 for the Fe-ore). Nevertheless, the highest costs would be obtained for the case where no fly ashes were generated (6-8.1 €/ton CO_2 for ilmenite, 0.9 €/ton CO_2 for Fe-ESF and 4.2-6.2 €/ton CO_2 for the Fe-ore). The low cost per ton of CO_2 obtained with all of the Fe-based oxygen carriers reinforces the potential of the CLC technology as an advantageous carbon capture technology.

4. Conclusions

This paper evaluates the environmental impact of the disposal in a landfill of different oxygen carriers commonly used in CLC of coal. These carriers are Fe-based materials: ilmenite, a bauxite residue (Fe-ESF) and an iron ore (Fe-ore).

Lixiviation tests were performed with the bed materials and the fines recovered in the operation of a continuous 500 W_{th} CLC unit burning a bituminous Colombian coal. The lixiviation test followed the standard procedure set by the Council decision 2003/33/EC. According to the results obtained, ilmenite and the Fe-ore can be classified as stable nonreactive hazardous waste and disposed in the same type of landfill. The main environmental concern arose from the high chromium content of the bauxite waste residue (Fe-ESF). The concentration of this metal found in the eluates of the fines collected exceeded the PLV recommended and therefore, the used Fe-ESF oxygen should be disposed in a landfill for hazardous materials

An estimation of the residues of oxygen carrier generated per year and per 1 MW_{th} in a CLC unit was also done. The final amount of residues generated depended on the fly ashes in the coal used. If no fly ashes are generated, then the amount of solid residues produced would be 240 t/year·MW_{th} for ilmenite, 263 t/year·MW_{th} for Fe-ESF and 247 t/year·MW_{th} for Fe-ore. In this case, the fines collected at the outlet of the reactors would be oxygen carrier particles that could be used in similar applications as they were used originally (i.e. pigments). Otherwise, if all the ashes from coal were fly ashes, the total amount of residues generated would correspond to the sum of the losses in attrition (12 t/year for ilmenite, 32 t/year for Fe-ESF and 16 t/year for Fe-ore) and the ashes generated from this bituminous coal (115 t/year). In this case, the fines recovered after the filters can be considered as mainly coal ashes and then be used in the same reutilization processes as the ashes produced in power generation units

An estimation of the cost of the makeup flow of Fe-based oxygen carries per ton of CO_2 avoided in the CLC process was also made. Results for the case where no fly ashes are generated from coal indicated a cost between 0.9 and 8.1 €/ton CO_2.

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List of Figure captions

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

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

Figure 3. Concentration of Cd and Cr in the eluate obtained in the lixiviation of a Fe-ESF sample used in the CLC continuous unit and the corresponding fines under (A) L/S ratio = 2 and (B) L/S ratio = 10. Dashed lines represent the proposed limit values (PLV) according to the European Council Decision 2003/33/EC

Figure 4. Estimation for different fly ash percentages in coal of (A) the tonnes of total residues generated per year in a 1 MW_{th} CLC plant (B) percentage of oxygen carrier in the solids recovered in the filters (C) cost of the makeup flow of the Fe-based oxygen carriers per ton of CO_2 avoided

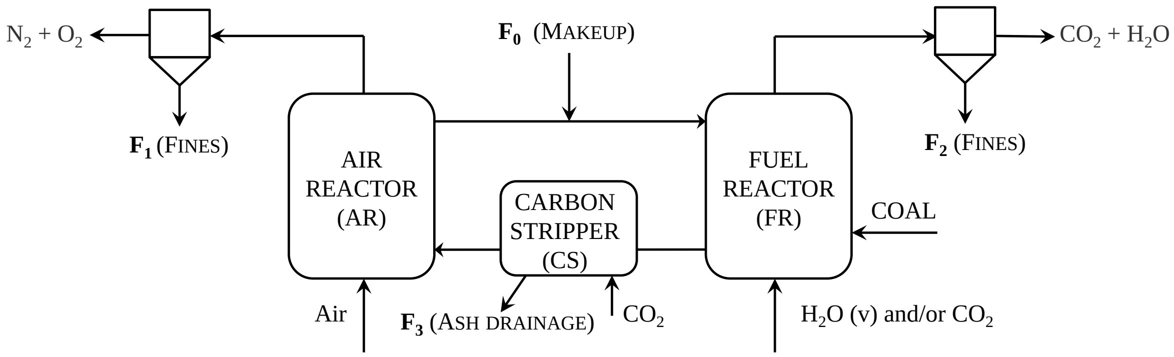
$N_2 + O_2$
F_0 (MAKEUP)
$CO_2 + H_2O$
F_1 (FINES)
AIR REACTOR (AR)
FUEL REACTOR (FR)
F_2 (FINES)
CARBON STRIPPER (CS)
COAL
Air
F_3 (ASH DRAINAGE)
CO_2
H_2O (v) and/or CO_2

Figure 1.

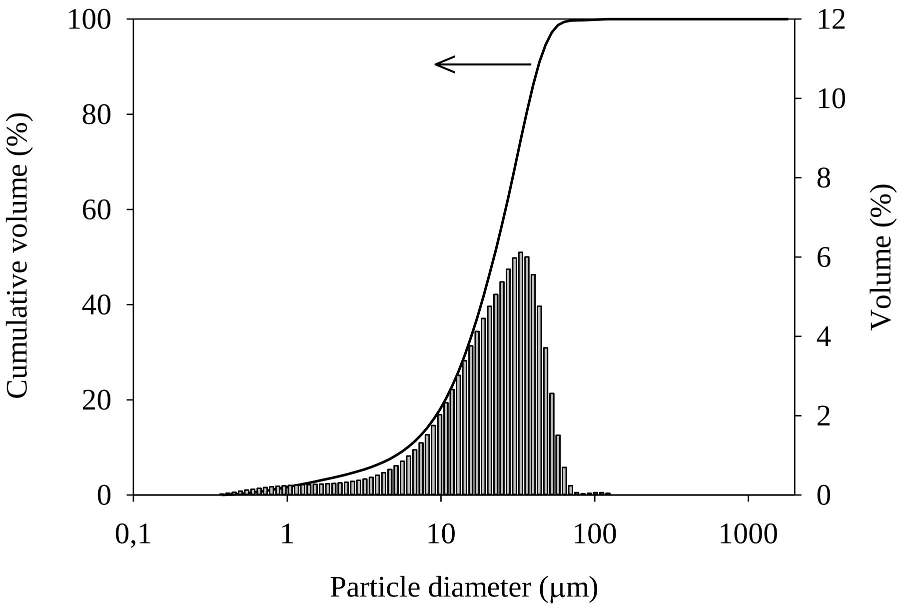
100
80
60
40
20
0
Cumulative volume (%)
12
10
8
6
4
2
0
Volume (%)
0,1
1
10
100
1000
Particle diameter (µm)

Figure 2.

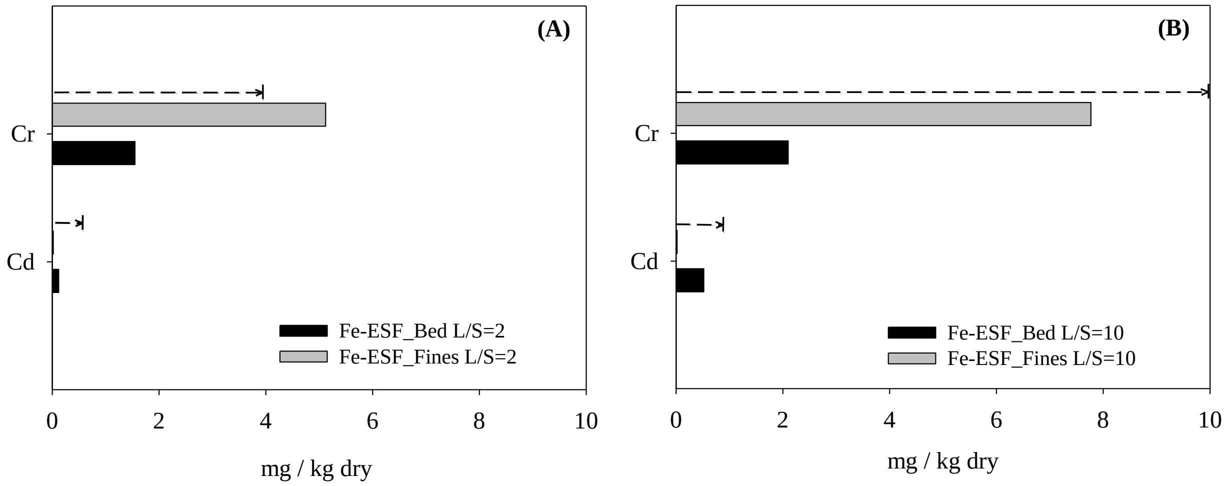
(A)
Cr
Cd
Fe-ESF_Bed L/S=2
Fe-ESF_Fines L/S=2
0
2
4
6
8
10
mg / kg dry
(B)
Cr
Cd
Fe-ESF_Bed L/S=10
Fe-ESF_Fines L/S=10
0
2
4
6
8
10
mg / kg dry

Figure 3.

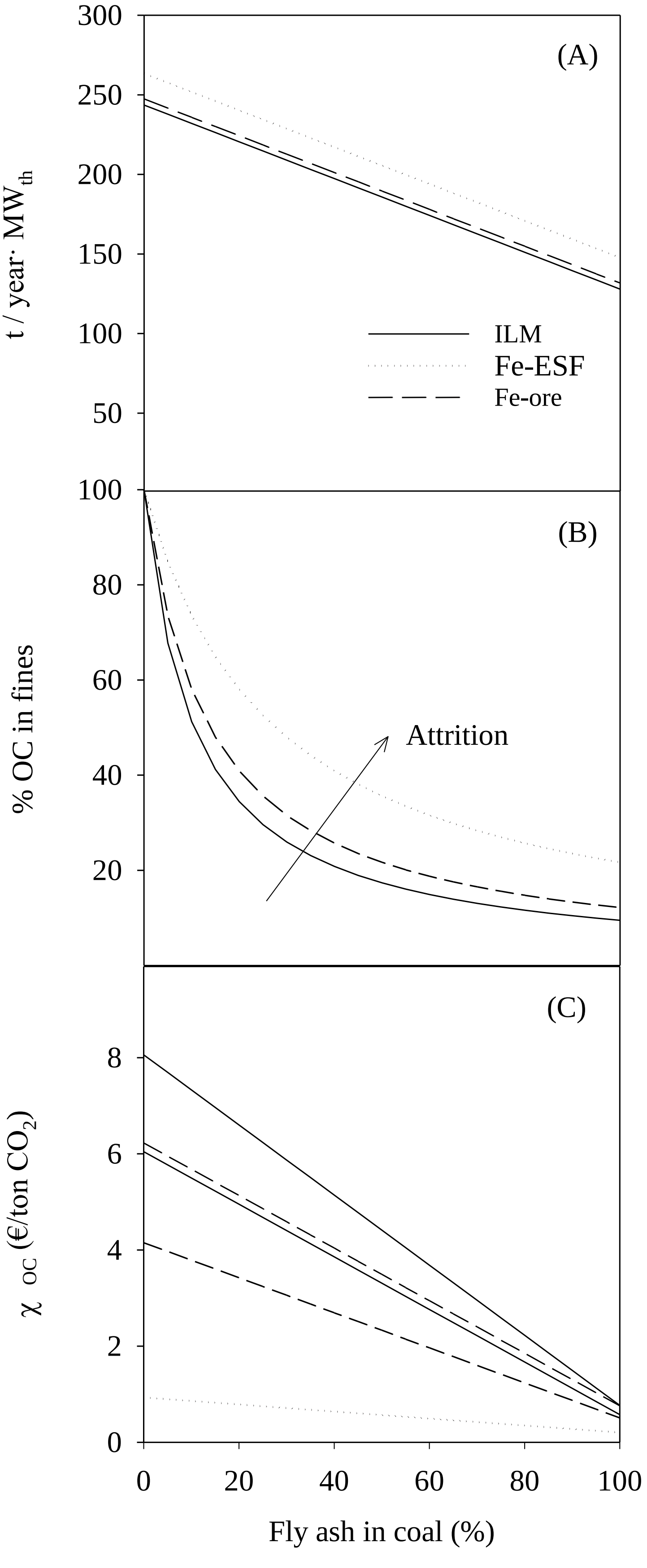
(A)
t / year· MW$_{th}$
300
250
200
150
100
50
ILM
Fe-ESF
Fe-ore
(B)
% OC in fines
100
80
60
40
20
Attrition
(C)
χ OC (€/ton CO$_2$)
8
6
4
2
0
0
20
40
60
80
100
Fly ash in coal (%)

Figure 4.

Tables

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)	21900

Table 2. Composition of ilmenite (ILM), the bauxite waste (Fe-ESF) and the iron ore (Fe-ore) in the different streams of the CLC unit

			Composition (wt.%)														
Stream	**Sample**	**dp (μm)**	**Al**	**Ca**	**Cd**	**Cr**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Si**	**Ti**	**V**	**Zn**
F_0	**ILM_c**	150 - 300	0.55	0.37	0.01	0.12	51.60	0.15	3.38	0.31	0.19	0.05	0.13	1.63	41.33	0.15	0.02
F_1+ F_2	**ILM_f**	< 40	4.93	1.60	0.01	0.23	49.91	0.12	4.16	0.46	0.23	0.15	0.04	6.59	31.33	0.18	0.07
F_3	**ILM_b**	150 - 300	0.98	0.46	0.01	0.11	52.73	0.00	3.74	0.32	0.08	0.04	0.03	1.96	39.33	0.17	0.03
F_0	**Fe-ESF_c**	100 - 300	19.57	0.67	0.00	0.35	69.58	0.26	0.08	0.04	4.52	0.03	0.03	1.08	3.67	0.10	0.03
F_1+ F_2	**Fe-ESF_f**	< 40	14.38	1.24	0.01	0.49	69.48	0.34	0.34	0.11	4.13	0.17	0.03	5.31	3.62	0.34	0.03
F_3	**Fe-ESF_b**	100 - 300	18.52	0.63	0.00	0.32	70.79	0.22	0.11	0.07	3.58	0.02	0.03	1.85	3.70	0.12	0.03
F_0	**Fe-ore_c**	100 - 300	3.12	4.99	0.01	0.16	81.68	1.34	2.71	0.07	0.08	0.02	0.01	5.68	0.11	0.01	0.00
F_1+ F_2	**Fe-ore_f**	< 40	3.64	11.15	0.02	0.07	71.57	0.78	5.68	0.03	0.02	0.02	0.28	6.32	0.36	0.04	0.02
F_3	**Fe-ore_b**	100 - 300	3.21	1.90	0.02	0.13	85.91	0.92	1.36	0.07	0.04	0.02	0.04	5.76	0.59	0.03	0.02
Ash	**Bituminous coal**	< 75	18.59	4.95	0.02	0.04	13.15	3.09	3.39	0.17	1.59	0.15	0.05	53.75	0.92	0.08	0.06

_c: calcined; **_f**: fines; **_b**:bed

Table 3. Proposed limit values (PLV) for Cd, Cr, Ni, Pb and Zn in the eluates and corresponding results for the different oxygen carrier streams in the continuous CLC unit and the ash sample. All values are expressed in mg/ kg dry matter. Shaded values exceeded the PLV

Sample	**Stream**	**L/S (L/kg)**	**Cd**	**Cr**	**Ni**	**Pb**	**Zn**	**Average pH**
PLV		2	0.6	4	5	5	25	≥ 6
		10	1	10	10	10	50	
ILM_f	**F_1+ F_2**	2	0.12	0.10	-	-	-	7.0
		10	0.62	0.82	-	-	-	
ILM_b	**F_3**	2	0.10	0.12	0.02	0.00	0.04	9.4
		10	0.5	0.44	0.10	0.00	0.20	
Fe-ESF_c	**F_0**	2	0.20	20.76	0.04	0.08	0.10	10.5
		10	0.68	25.20	0.12	0.16	0.34	
Fe-ESF_f	**F_1+ F_2**	2	0.02	5.12	0.06	0.00	0.00	11.0
		10	0.02	7.77	0.22	0.00	0.00	
Fe-ESF_b	**F_3**	2	0.12	1.55	0.02	0.04	0.06	11.0
		10	0.52	2.10	0.10	0.12	0.22	
Fe-ore_f	**F_1+ F_2**	2	0.13	0.21	-	-	-	12.7
		10	0.64	1.16	-	-	-	
Fe-ore_b	**F_3**	2	0.10	0.26	0.02	0.02	0.04	11.7
		10	0.50	0.66	0.10	0.10	0.20	
coal ash		2	0.00	0.64	0.04	0.00	0.00	11.8
		10	0.00	1.62	0.22	0.00	0.00	