AFBC of coal with tyre rubber. Influence of the co-combustion variables on the mineral matter of solid by-products and on Zn lixiviation

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\section*{Abstract}

The study focuses on the generation and distribution of mineral species in fly and bottom ashes. These were formed during a fluidised co-combustion of a fossil fuel (coal) and a non-fossil fuel (tyre rubber) in a small fluidised bed combustor (7 cm × 70 cm). The pilot plant had continuous fuel feed using varying ratios of coal and rubber.

The study also focuses on the lixiviation behaviour of metallic elements with the assessment of zinc recovering.

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1. Introduction

The recovery and re-use of waste products are high priorities in today's markets due to price increases in raw materials and the global energy crisis. This is very much the case with end-of-life tyres [1-3]. In 2008 the European Union generated approximately 1.3 million tonnes of tyre, with Spain contributing 340,000 tonnes [4]. The re-use of waste products is financially attractive [5] as it reduces fuel consumption, land fill usage, energy costs and of course reduces the amount of waste material. During this 2008 year Europe re-used approximately 32% of tyres via waste-to-energy [4], providing a high calorific value non-fossil fuel (28–38 MJ/kg) [6] with a low mineral content [7].

The main pollutants emitted from the co-combustion of tyre with coal are: solid particles, non-condensable gases (carbon monoxide, sulphur dioxide, nitrogen oxides), trace elements and organic compounds (Polycyclic aromatic hydrocarbons and chlorobenzenes) [7,13].

This non-fossil fuel can contribute between 10% and 25% of the initial fuel mixture during co-combustion [14], depending on the fuel content and the Ca/S ratio used for the desulphurisation process.

In 2007 the 15 member states of the European Union produced over 61 million tonnes of coal ashes [15]. These ashes can contain toxic metals, such as mercury, lead, cadmium, chrome, nickel and manganese. The concentration of these metals in the ashes will largely depend on the combustion conditions and the atmospheric pollution control devices [16]. In addition, the toxic metal content of fossil fuels will vary due to geological and geographical factors relating to the composition of the coal or petroleum deposits [17]. The toxic metal content of waste material combustion will vary, depending on the type of waste used [18,19].

Fly ashes and bottom ashes, solid by-products of combustion, show different characteristics [20]. Fly ashes tend to represent a greater environmental impact due to their composition, where trace elements are mainly enriched in non-magnetic, heavy and fine-grained fractions.

The classification of bottom ashes as toxic waste will depend on their heavy metal content [16]. The varying thermal stability of different heavy metals will determine their distribution after combustion. Metals with low volatility, such as titanium, chromium, copper or nickel (in the absence of chlorine) largely remain in the bottom ash; a small proportion may be elutriated in the fly ashes as small particles. The bottom ash content of other semi-volatile metals, such as cadmium, lead and zinc (in the presence of chlorine) is greatly reduced [21] as they will tend to boil off, depending on the atmospheric conditions in the combustion system. Subsequent temperature reduction of these gasses leads to the metals collecting in the fly ash, kept back by the particle uptake systems. Some metals, such as lead and cadmium, are more abundant in fly ash due to their higher volatility and greater porosity relative to other metals. This increases the toxicity and lixiviation risk of ashes. The very high volatility of mercury allows it to be almost completely boiled off and so mercury does not usually constitute a problem with bottom ash.

Different hydrometallurgical procedures were assessed for the recovery of secondary zinc-rich by-products [22]. These procedures are considered to be environmentally acceptable, with the derived-by-products suitable for safe disposal. The possible recovery of lead and zinc from ashes produced via incinerating municipal solid waste [23] was studied. The chemical composition of the ashes was identified using different techniques (XRD, SEM, AAS). Other authors suggest a hydrometallurgical and pyrometallurgical procedure to recover zinc from secondary resources, such as worn-out batteries, scrap metal, zinc slag and zinc rich ashes, resulting in 99% efficiency and an acceptable recovery cost [24]. Other metals, such as copper, zinc and lead, have been successfully recovered from smelting slag. This procedure used different acid and alkaline solvents and accompanied with the study of different impacting lixiviation parameters, reached a maximum performance of 98%. The results of a preliminary economic review show the operating costs are competitive [25]. Other authors analysed the lixiviation and zinc extraction behaviour of ashes obtained from the laboratory-scale furnace combustion of waste tyres, with zinc recovery results reaching 67% [26].

There has been further research on the lixiviating behaviour of fly ash from incinerating municipal solid waste (MSW). This research assessed the environmental impact for its disposal in dumps and also for the detoxification of metals or their recovery. In addition a lixiviation efficiency comparison was established with different reactants, such as hydrochloric acid, sodium hydroxide and water. It concluded that hydrochloric acid attains better results in the lixiviation of elements like cadmium, lead, zinc and potassium [27].

These procedures appear state of the art and so it seemed appropriate to study the mobility of inorganic species in the ashes. These result from the combustion of varying coal and tyre rubber mixtures (90%/10% and 30%/70% respectively). The ashes were produced under different combustion temperatures (750 °C and 850 °C) in a fluidised bed and were collected in the ash pan and cyclones. Particular attention was paid to zinc extraction, one of the main inorganic compounds present in tyre rubber [28], with the assessment of the possible economic interest of its recovery.

The use of end-of-life tyres as a non-fossil fuel, together with their co-combustion with coal of different ranks, has been widely reported [7–12].

The study is focussed on zinc partitioning between gaseous emissions (as a trace element) and solid products from the combustion of coal, tyres and blends of both fuels in different ratios. The highest zinc concentration was seen to be in the ashes. Zinc lixiviation from the ashes by hydrometallurgical techniques was intended to reduce environmental impact whilst increasing zinc compounds recovery. Zinc and its oxides are used in a wide variety of processes including the galvanising of iron and steel, the production of brass, laminates, as a catalyst in the production of synthetic rubber and in die cast alloys [22,29].

The atmospheric fluidised bed combustion (AFBC) pilot plant used allowed the combustion of different rank coals mixed with wastes of varied natures [7]. This combustion system shows several advantages over conventional systems, such as fuel flexibility and better emissions control. The work was carried out at relatively low combustion temperatures (750–850 °C), addressed to reduce NOx emissions and to avoid the ashes fusion.

The study also focus the lixiviation of zinc contained in coal combustion products (CCPs) and tyres, determining the influence of parameters such as temperature, lixiviation period, choice of reactants and their concentration [30,31]. X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques were applied for the characterisation of the CCPs. Metal identification was performed by means of atomic absorption spectroscopy (AAS).

2. Experimental

2.1. Ash samples

The fuel raw materials were a low-rank Spanish coal (classified as sub-bituminous and originating from the EMMA mine in Puerto-lina, with a 0.5–1 mm initial particle size) and a non-fossil fuel. The latter was a non-specific mixture of end-of-life tyre rubber (from which the steel wire had been removed) with a particle size of 1 mm. The characterisation of both raw materials was carried
out using an automatic LECO SC-32 analyser, to determine the total sulphur, using automatic analyser LECO CHN-600 for an elementary carbon, hydrogen and nitrogen analysis. Standard rules were followed to determine the remaining parameters, apart from standard ASTM 2492-90 for the determination of organic sulphur in the coal. The elemental and immediate analyses of both raw materials are shown in Table 1.

The combustions of the coal and tyre (isolated and their blends) were performed in a laboratory scale atmospheric fluidised bed reactor (size: 70 cm × 7 cm internal diameter), AFBC, whose characteristics have been already published [13]. The operating conditions were optimised and set at working temperatures between 750 ºC and 850 ºC, at an air speed of 0.245 m/s and 5% excess oxygen. Samples were taken at 2 h interval once steady-state operation was reached in the plant. The combustion products were collected in the cyclones (fly ash) and in the ash pan (bottom ash). Table 2 shows the different experiments carried out.

The results show the fuel characteristics for coal and tyre are very different:

- The ash content is greater in coal (41.46% as received) than in tyre (3.30% as received).
- Tyre has a much higher calorific value (38.82 MJ/kg) than coal (15.30 MJ/kg).
- Almost half the total sulphur content of coal is inorganic, whilst in the case of tyre is organic sulphur.
- The total zinc content in coal is very low (0.06%) in comparison with that of tyre (1.13%).

The products resulting from the different fuel proportions were characterised by a Philips PW-1404 X-ray Fluorescence Spectrometers, with a Sc–Mo tube. The crystalline phase identification was performed by X-ray Diffraction, using a Philips PW–1710 diffractometer with CuKα radiation, equipped with a graphite monochromator and an automatic divergence slit and operating at 40 kV. The mineralogical study was performed with a Hitachi S-570 scanning electron microscope including a Kevex 3500 microanalyser.

2.2. Lixiviation procedure

The lixiviation process used 2 g of the different solid combustion products, ground to less than 0.25 mm. The study looked at variables that could alter the effectiveness of the process, such as the choice and concentration lixiviant [22], the temperature and the operating time [30–31]. Lixiviation tests were carried out with different acid, alkaline and neutral reactants, such as sulphuric acid (H2SO4) at 11% and 20%, sodium hydroxide (NaOH) at 17% and 7.5%, 20% hydrochloric acid (HCl), 7% ammonia (NH3) and water (H2O). The lixiviation operation was carried out with continuous agitation (1200 rpm), at temperatures of 30 ºC, 50 ºC and 70 ºC, for periods of 10, 30 and 120 min.

The pulp was filtered out. The liquid and solid phases were qualitatively and quantitatively analysed by using Atomic Absorption Spectrometry (Philips 9.100X) and UV–VIS (Perkin-Elmer, Lambda 3 UV/VIS model).

3. Results and discussion

3.1. Characterisation of fuels and ashes nature

The mineral species present in the initial tyre were isolated by low-temperature ashing (LTA) in a high vacuum oxygen plasma reactor. This allowed analysis of the fuels mineral matter without any modification during the combustion process. Once the fuel organic matter was eliminated, the mineral matter was analysed by XRD pre and post lixiviation. Zincite (ZnO) was the main crystalline phase detected followed by a lower presence of calcite (CaCO3), some quartz (SiO2), (see Fig. 1a) and some kaolinite, smectite and illite (Fig. 1b). These compounds were due to the use of clays and zinc oxide as additives in tyre manufacturing.

Amorphous silica is the other main rubber component; it is found in similar percentages to those of zincite. This silica cannot be detected with X-ray diffraction as it is not in crystalline phase, although it is detectable with Fourier Transform Infrared Spectrometry (FTIR), (see Fig. 2). The characteristic of the Si–O bond can be observed at absorption bands at 1137 cm−1, 795.76 cm−1 and 467.60 cm−1.

Ashes from fixed bed combustion at 800 ºC have also been obtained and analysed for comparison with LTA. The main mineralogical compounds of the corresponding fixed bed ashes are zinc oxides and zinc silicates, originating from the reaction of zinc oxide

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental and immediate analysis of coal and tyre rubber.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture% (sample received)</td>
<td>7.49</td>
</tr>
<tr>
<td>Ash% (sample received)</td>
<td>41.46</td>
</tr>
<tr>
<td>CS (dry basis)</td>
<td>39.99</td>
</tr>
<tr>
<td>N% (dry basis)</td>
<td>0.93</td>
</tr>
<tr>
<td>S% (dry basis)</td>
<td>0.96</td>
</tr>
<tr>
<td>HI% (dry basis)</td>
<td>3.17</td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
<td>15.30</td>
</tr>
</tbody>
</table>

| Table 2 | Experiments in the atmospheric fluidised bed plant with different fuel mixtures at different combustion temperatures (v = 0.245 m/s and 5% excess O₂). |
| --- | --- | --- |
| Coal (%) | Tyre rubber (%) | Temperature (°C) |
| 100 | 100 | |
| 90 | 10 | 750, 800, 850 |
| 70 | 30 | |

Fig. 1. Diffractograms of: (a) rubber ash obtained by low temperature ashing (100–150 ºC). (b) The same ashes after lixiviation with H2SO4 2.3 N (30 ºC). The principal peaks marked: Q = quartz, Z = zincite, C = calcite, K = kaolinite, I = illite, S = smectite.
with silica or silicates. For this ash, kaolinite bands do not appear in the diffractogram, although they are detected in the original tyre analysis by FTIR. That could be due to its conversion to metakaolinite, due to the higher temperatures reached in fixed bed.

Table 3 gives information on ashes from AFBC of tyre and coal ashes and those from their different ratio mixtures. The main inorganic compounds of rubber are silica and zinc oxide, used respectively as a reinforcing and accelerating load in tyre vulcanisation. Thus the most prevalent metallic compounds detected in these tyre ashes are silica dioxide (SiO₂) and zinc oxide (ZnO). Zinc, due to its volatility, is distributed among the bottom ashes collected in the ash pan as well as the fly ash collected in the cyclones. Nickel is present in very low levels in coal but at significant levels in tyre rubber. Due to the low ratio of rubber tyre/coal used (0.10 or 0.43) and the low percentage of tyre ashes the main inorganic compounds in the mixture coal/tyre ashes are silicates, from the coal and tykes, and aluminium oxide, from the coal. Zinc oxide is the only inorganic compound present in tyres (1% approximately) that increases notably in tyre ashes from AFBC reaching 32.34%, but in the mixture coal/tyre ashes, the final contents in all studied ratios was always under 1%. Silica dioxide (SiO₂), aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) represent approximately 90% of all ashes. As previously commented the ashes from the coal–rubber mixture (with a high percentage of coal) have a very similar composition to those of coal ashes, the major difference being level of zinc.

The comparison of fly ash with bottom ash collected in the ash pan (Table 3), produced from 90% coal and 10% tyre rubber, shows a general, slight reduction of all elements. The exception, with a slight increase, is zinc. This increase is due to its volatility and to the presence of carbonaceous material in the fly ash. This material is elutriated in the gaseous current as part of the fly ash collected by the cyclones. Table 4 shows that when tyre is burnt by itself the fly ashes have an increased quantity of organic matter and the content of mineral matter is lower than those from the bottom ashes (see Table 3 for comparison) due to the presence of a significant amount of unburned particles (expressed as% organic matter).

A series of solid deposits (slaggings) appear on the walls of the reactor during the combustion of tyre rubber due to the agglomeration of ash particles. These cause operational problems and affect the availability and thermal efficiency of tyre combustion as they modify the fluidisation. The mineral matter of this slag has been analysed (Table 5) in an attempt to understand the mechanisms of its formation and therefore so to prevent them forming. In order to facilitate the follow up study of the mineral matter, the limestone was not added to the reactor, usually employed to control inorganic emissions during combustion. This avoided diluting the ashes and modifying the behaviour of inorganic components during combustion. Comparing the slag analysis in Table 5 with the tyre bottom ash and tyre muffle ash analysis in Table 3, it can be deduced that the slag is highly enriched by Fe, Ni and Cr and highly impoverished by Si. This leads to the formation of franklinite and other species containing zinc. To diminish these reactions between the grains of tyre ash it can be useful to dilute the tyre grains with grains of an inert or near inert substance in these conditions, as can be silica or alumina grains. When the mixture of tyre and coal is burnt, coal ashes grains act as a diluent and the slag is not formed.

The particle sizes of all the combustion products were measured and recorded. Fig. 3 shows the granulometric analysis of the fly ash, and the bottom ash, resulting from the combustion of coal and tyre mixtures. They were produced using different coal/rubber ratios (90/10 and 70/30) and at different temperatures (750 °C and 850 °C). The results show approximately 80% of fly ash particles are less than 0.1 mm in size, whilst 80% of bottom ashes are less than 0.4 mm. These smaller particles of fly ash, with respect to bottom ashes, lead to an increase to their surface-area-to-volume ratio and by consequence a high reaction rate during the lixiviation.

3.2. Influence of combustion variables on inorganic species

It should be noted that ash, due to the combustion temperature and the reaction time, is a product whose mineralogical compo-

![Fig. 2. FTIR spectrum of tyre ashes by low temperature ashing (100–150 °C) LTA, liquidized with H₂SO₄ 2.3 N (30 °C).](image-url)
Table 4

| Oxides (%) in the fly ash from AFBC rubber tyre (ν = 0.245 m/s and 5% excess O₂) at different temperatures. |
|--------------------------------------------------|------------------|------------------|------------------|
| 750 °C  | 800 °C  | 850 °C  |
| Fe₂O₃   | 0.98   | 0.98   | 1.41  |
| CaO     | 0.72   | 1.01   | 1.08  |
| MgO     | 0.79   | 1.11   | 1.26  |
| P₂O₅    | 0.331  | 0.575  | 0.582 |
| K₂O     | 0.22   | 0.37   | 0.37  |
| Na₂O    | 0.25   | 0.42   | 0.39  |
| ZnO     | 9.18   | 13.55  | 12.30 |
| Cr₂O₃   | 0.01   | 0.01   | 0.01  |
| NiO     | 0.060  | 0.045  | 0.043 |
| CoO     | 0.010  | 0.014  | 0.012 |
| MnO     | 0.010  | 0.015  | 0.018 |
| PbO     | 0.018  | 0.025  | 0.025 |
| CuO     | 0.010  | 0.010  | 0.017 |
| % MM    | 17.99  | 32.47  | 34.63 |
| Organic matter | 82.01 | 67.53 | 65.37 |

Table 5

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Tyre rubber slag 800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>19.83</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.59</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>23.78</td>
</tr>
<tr>
<td>CaO</td>
<td>6.42</td>
</tr>
<tr>
<td>MgO</td>
<td>1.41</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.38</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.54</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.68</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.48</td>
</tr>
<tr>
<td>ZnO</td>
<td>22.13</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.51</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>9.33</td>
</tr>
<tr>
<td>NiO</td>
<td>10.77</td>
</tr>
<tr>
<td>CoO</td>
<td>0.0</td>
</tr>
<tr>
<td>MnO</td>
<td>0.25</td>
</tr>
<tr>
<td>PbO</td>
<td>0.0</td>
</tr>
<tr>
<td>CuO</td>
<td>0.0</td>
</tr>
<tr>
<td>% MM</td>
<td>100</td>
</tr>
</tbody>
</table>

The evolution of mineralogical species during tyre combustion in both fluidised bed and muffle furnace (as special “fixed bed”), was studied to compare the influence of the different combustion conditions as demonstrated in the diffractograms of Fig. 4a and b. It is worth pointing out that, where tyre alone was combusted in fluidized bed, three solid products are generated: fly ashes, pan ashes and “incrustation” ashes, produced by agglomeration of ash particles. In the pan ashes from fluidized bed combustion (Fig. 4a) a predominance of the willemite (Zn₆SiO₄) mineral phase in comparison with zincte can be observed. However, the peaks in the mineral phase for hardystonite (ZnCa₂Si₂O₇) are negligible here. When tyre rubber is burned in a muffle furnace, (Fig. 4b), there are no relative movements or segregations. Its residence time is greater and the temperature more uniform, transforming zincte into willemite. This in turn transforms into hardystonite to a certain extent, due to the attack on zincte by the silica phases. In fluidised bed combustion, shorter residence times and greater temperatures can be reached locally, affecting the evolution of the elements that are in contact within the same grain. These facts promote the formation of fly ash and also incrustations in which the amount of hardystonite is greater (together with that of chrome and nickel), particularly due to these incrustations longer residence times.

Fig. 5 shows an SEM image of a grain of the pan ashes (800 °C, AFBC) with different inclusions (a). The square area selected is amplified in (b). It shows that the willemite formation is due to the attack of silicates on zincte and some willemite grains shows inside a zincite residue.

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Fig. 3. Granulometric analysis of the by-products from the combustion of coal and tyre mixtures, 90/10 and 70/30 ratios, at 750 and 850 °C.

Fig. 4. Diffractogram of the bottom ashes from AFBC of the tyre rubber at 800 °C (a) and in muffle furnace (b); ν = 0.245 m/s and 5% excess O₂. W = willemite, Q = quartz, Z = zinc oxide, A = anhydrite, H = hardystonite and Mag = magnetite type phases.
The fly ashes generated in the tyre rubber combustion in the fluidised bed plant are collected in the cyclones. The tyre rubber fly ash composition varies significantly from the ashes collected in the ash pan. In the diffractogram of the fly ash produced at 800 °C (Fig. 6) it can be observed how the most important crystalline phase is zirconite, followed to a much lesser extent by a willemite phase, whose corresponding peak can only be appreciated in those from combustion at 800 °C and 850 °C but not at 700 °C. A very scarce quartz phase can also be seen. This could be due to the short residence time in the fluidised bed reactor, which is not enough to reach the temperature for reactions between the silica phases, the iron oxides and the zinc compounds.

There is particle fragmentation due to friction in the bed, where the small particles can be elutriated outside the combustion reactor together with the fly ash. The organic matter contents found in the fly ashes can be high, particularly in the case of combustion at 750 °C, and for this reason the density of these fly ashes is lower by comparison with those collected in the ash pan. Therefore, they can be dragged quickly throughout the reactor, avoiding possible mineral transformations. In order to corroborate this result, the fly ash produced at 850 °C was subjected to lower temperature combustion (750 °C) for several hours in a muffle furnace, resulting in a solid showing a completely different diffractogram (Fig. 7) to the one studied previously (Fig. 6) but very similar to that obtained with the bottom ashes from the ash pan (Fig. 4a), where the willemite peaks are now very intense and even very tenuous hardystonite peaks also appear.

The evolution of mineral species from the tyre rubber/coal mixture during combustion was tested using bottom ashes in a proportion mixture of 70% coal–30% tyre and 90% coal–10% tyre at 750 °C (Figs. 8 and 9). The results were very similar to the ones obtained when using coal ashes (Fig. 10). The crystalline phases are quartz and mica. We detected anhydrite and hematites phases when the ankerites and siderites from coal decompose. This similarity comes from the low content of ashes in the tyre and the high content of ashes in the coal resulting in near the same amount of ashes as in the coal ashes. When comparing the analysis of AFBC coal bottom ashes with the bottom ashes obtained from 70% coal–30% tyre and 90% coal–10% tyre blends, it shows the variations of Zn, Cr and Ni are very low.

The bottom ashes from 90% coal/10% tyre mixture were analysed by SEM to check the inorganic species in detail. The majority of the grains correspond to coal ashes (iron oxides, silica, calcium compounds, silicates) with only a few generated from the tyre ashes. Fig. 11a shows the SEM image of an ash grain from the tyre rubber of the mixture. The square areas marked (a1 and a2) are amplified in Fig. 11a1 and a2. Grains of willemite, magnetite type phases and others grains adsorbing elements as, for example, zinc, can be observed.

An example of a coal particle that comes from the 90% coal/10% tyre mixture is shown in detail in Fig. 12a and b. It can therefore be assumed that the image is clearly from a coal particle, as it still has a pyrite “framboid” already transformed into ferric oxide. The mineral species present are calcium sulphates with some iron and manganese, calcium carbonate, alumina-silicates and iron oxide.
Calcium sulphate could have originated from the mineral or as a consequence of the reaction between the sulphur oxides produced by the sulphides present in coal.

There is a suggestion, from the scanning electron microscope study, that in the co-combustion of the 90% coal/10% tyre mixture in AFBC, the grains of each component tend to preserve their individual nature. This leads to no significant interaction or transfer of matter between the different types of mineral residues. It further suggests that in the lixiviation, each type of grain would behave as though typical of the fuel it originated from. It is important to highlight the non-uniformity of the grains of coal and tyre. When the tyre is predominant the tyre grains interact and can add to the scoria production (possibly due to their low melting point) as it is discussed in the next paragraph.

Studying the formation of scoria or slaggings from tyre combustion should include elucidating the evolution of the species in order to understand their formation and, thus, to try to avoid them. Previous to this publication, the slag produced during tyre combustion at 800 °C in the fluidised bed plant [32] was analysed using XRD. It was reported that magnetite and other minerals such as franklinite and chromite. Zincite, willemite and hardystonite were also found in the bottom ash (Fig. 4). Now, by using SEM (Fig. 13), it is possible to visualise the mineral species, their interrelation with the different phases and to analyse them in a specific manner. This shows the evolution of the species in the slag generated in tyre AFB combustion at 800 °C. The willemite and zincite presence was confirmed, by X-ray diffraction, together with the presence of hardystonite. A zincite grain in its central part can be seen in Fig. 13. In turn, this phase is surrounded by willemite and them by hardystonite. This evolution conducts to more difficult leaching species than the zincite.

3.3. Lixiviation process and zinc recovery from the tyre and tyre/coal mixture ashes

After analysing the effectiveness of zinc extraction by different lixivants under the same working conditions, it was proved that:

- Acid agents were more effective than alkali agents.
- Sulphuric acid (at both concentrations) and hydrochloric acid gave a recovery rate over 90% in the solution.
- Sodium hydroxide (NaOH) and ammonia (NH₃) have respective recovery rates of 31% and 5%.
- The water lixiviation test showed zinc to be absent.

Sulphuric acid was shown to be more appropriate for zinc recovery than hydrochloric acid [22] due to its higher application in the metallurgical industry and greater zinc selectivity. Hydrochloric acid partially dissolves other elements; this may have a negative influence on zinc electrolysis.

The influence of the different lixivants in zinc extraction is shown in Fig. 14. The solution and the solid product obtained from lixiviation were analysed using AAS. The results of lixiviation are expressed as the percentage zinc recovered in the solution with regard to the original content of the sample.

Following from these results sulphuric acid was used as the lixiviating agent of choice, at different temperatures and for different time periods. The results, expressed as zinc recovery rate and zinc content in solid residue of the sample, are shown in Table 6. An increase in zinc solubility as the lixiviation time and temperature increase can be observed. The maximum zinc extraction was obtained with a temperature of 70 °C for 120 min, reaching approximately 96% with 20% concentration of sulphuric acid. There was very little difference (1%) in the percentage recovery of zinc between the two concentrations of sulphuric acid used.

For the metals nickel and iron: the amounts recovered via acid lixiviation were very low compared to those with zinc (given the same time and temperature conditions) (see Table 6), as can be seen in Fig. 15. For calcium, partial dissolution was observed, resulting in maximum values of 46% with the highest operating conditions of temperature and time. This is likely due to the low solubility of calcium sulphate in sulphuric acid. Temperature and
Fig. 11. SEM microphotograph of the bottom ashes from the AFBC of the 90% coal/10% tyre rubber mixture at 750 °C, v = 0.245 m/s and 5% excess O₂. Si-Ca = calcium silicate absorbing zinc, Si-M = silicate absorbing phosphorous, potassium, calcium, iron and zinc; Z = zincoite, MAG = magnetite type phases, W = willemite.

Fig. 12. SEM microphotograph of the bottom ashes from AFBC of the 90% coal/10% tyre rubber mixture at 750 °C. CaCO₃ = calcium carbonate, CaSO₄ = calcium sulphate, Al-Si = aluminosilicates, Fe₂O₃ = ferric oxide.
time were the parameters with the greatest influence on recovery. For magnesium it was seen that maximum extraction values of approx. 65% were reached, without time or temperature having any influence. For all these metals referred, the same leaching tendencies were confirmed using a lower acid concentration of 11%.

Zinc recovery depends on the combustion temperature and the ash type. As the combustion temperature is higher the more difficult becomes the zinc recovery. Besides, when fly ashes are elutriated, they are exposed less time in the reactor and as consequence their temperature is lower than the temperature of the bottom ashes. As fly ashes reaction time is shorter, its mineral material suffers less evolution which makes zinc recovery much easier. Fig. 16 shows results of zinc recovery from fly ashes obtained through AFBC combustion when mixing 70% coal/30% tyre and 90% coal/10% tyre exposed at 750 °C and 850 °C respectively. (On the left are the results of 70%/30% coal/tyre and on the right the results for 90%/10% coal/tyre mixture). Both blends show that when combustion temperature increases, the zinc extraction decreases. During the lixiviation process, temperature has great impact on zinc extraction. The extraction is easier when increasing temperature from 30 °C to 70 °C compared to time testing (10 min and 120 min). One of the reasons is that at 70 °C is when the acid begins attacking zinc minerals such as: franklinite (with magnetite mineral structure), hardystonite, willemite. Another reason is that the silica acid generation can hinder the continuation of the attack and as a consequence the completion of zinc extraction becomes longer.

Fig. 17 shows the results for the pan ashes. These ashes have been kept longer at high temperatures and the zinc has been transformed more into less lixiviable mineral phases. The influence of the combustion temperature is apparent; in the two coal/tyre proportions shown the zinc extraction is lower at 850 °C than at 750 °C. The presence of more difficult lixiviable phases give lower zinc extraction in practically all cases with respect to the fly ashes, as shown in Fig. 16. These also increase the production of silica acid during the lixiviation, leading to the time being more influential, especially at 70 °C due to the gelatinous nature of this acid. The influence of the coal/tyre ratio is more complicated. At a combustion temperature of 850 °C the trend is the same as with the fly ashes; the recovery at 90% coal/10% tyre is lower than that at 70% coal/30% tyre. At 750 °C the results are different and the zinc extraction at 90/10 is better than at 70% coal/30% tyre. This is partly explained by the influence of the time of lixiviation being relatively higher at 70 °C and 120 min 70% coal/30% tyre than at 70 °C and 120 min. 90% coal/10% tyre. This suggests that there are more difficult zinc compounds to lixiviate. This can be explained as, at this temperature, the interaction between tyre particles and coal particles is less important than between the tyre particles themselves, as have been proved by the scoria formation in the combustion of only tyre particles. Tyre particles interaction
Fig. 15. Results of the lixiviation of different metals (except Zn) using 20% H₂SO₄ with tyre ashes from AFBC at 800 °C.

Fig. 16. Influence temperature and time of lixiviation on the zinc extraction (11% H₂SO₄ solution) of fly ashes from different coal/tyre mixtures obtained at different temperatures of combustion (% Coal, % Tyre).

Fig. 17. Influence temperature and time of lixiviation on the zinc extraction (11% H₂SO₄ solution) of bottom ashes from different coal/tyre mixtures obtained at different temperatures of combustion (% Coal, % Tyre).
between themselves is more likely at a mixture of 70% coal/30% tyre than at 90% coal/10% tyre due to the important significant dilution factor. A higher temperature of 850 °C leads to more interactions and diffusion of zinc into other substances.

In summary: the lixiviation tests on the ashes from fluidised bed of coal/tyre blend combustion show the mineral species behaviour in the lixiviation is characterised by the individual nature of the grains. This is shown in the SEM study of the ashes from the 90% coal/10% tyre mixture at 750 °C, (Figs. 11 and 12), where each mineral species behaves according to its origin. There is a noticeable zinc recovery from the AFBC coal/tyre rubber ashes, where their mineral species detected by SEM originate entirely from the tyre, with their behaviour regarding sulphuric acid remaining along the same lines as in the case of tyre rubber burned in the muffle furnace.

In view of the results obtained from the study of zinc recovery by hydrometallurgy techniques such as leaching, we recommend the following valorisation process of these wastes of combustion materials taking some previous steps to optimize the process: As a first step we must optimise the mix of raw materials, with the double aim of increasing the zinc content of the ash to be valorised and reducing the leaching of undesirable elements. In addition, another goal to be met is to reduce the formation of slag during the combustion process. Mixtures candidates for this process can be tyre rubbers and coals with lower% ash content, or even burning tyre rubber only using an inert diluent such as silica or alumina, which are substantially non-leanachable and avoid the formation of slag.

The leaching process proposed, would consist of several upstream stages, so that the new acid is used in the last stage of solid inert-leaching coming from previous stages of leaching, and beside the enriched solution with zinc is virtually neutralized with the initial ash incoming stream. The final operation would consist on the precipitation of zinc as a compound with an acceptable level of impurities that can be recycled in metallurgical companies involved in recycling. There is also the possibility of trying to recover the zinc as zinc sulphide precipitated from the final weak acid solution of the last lixiviation step and sent to the zinc metallurgies. Of course, this entire process of valorisation waste for zinc recovery would require careful economic assessment.

4. Conclusions

(a) The conversion of tyres to energy in an atmospheric fluidized combustion offers the advantages of a high calorific power and a minimum moisture and mineral matter content, making it a proper fuel to generate energy when mixed with other fuels e.g., high ash coals.

(b) The coal/rubber mixtures combustion leads to higher zinc concentrations in fly ash than in bottom ash. In addition, the higher the combustion temperature, the lower the zinc solubility, independently the ash be fly or bottom.

(c) The zinc recovery of fly ash from the coal/rubber mixtures is always greater than from bottom ashes due to the smaller evolution of zinc mineral species in the fly ash.

(d) Acid lixiviation provides the best zinc extraction results. By increasing lixiviation time and temperature an increase in zinc extraction is observed.

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References


