

## Article

# Development of a Sustainable Metallurgical Process to Valorize Copper Smelting Wastes with Olive Stones-Based Biochar

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**Abstract:** Flue dust waste coming from a copper (Cu) smelting company has been valorized using a newly developed metallurgical process with the aim of recovering a dust concentrated in valuable metals, such as lead (Pb) and zinc (Zn), and studying the feasibility of replacing anthracite with biochar as reducing agent. Metallurgical trials using different mixtures of reducing agents have been performed in a furnace at 1400 °C. This furnace employs a high-power thermal plasma (HPTP) system as energy source. Using copper as the base metal, pellets containing a mixture of the waste, different reducing agents, and binder were introduced into the furnace for their dissolution. Recovery yields in the range of 45–85 wt.% for Pb and Zn were obtained in the flue dusts. All the trials proved the effectiveness of the developed process to enrich the flue dusts in valuable metals, including those only using biochar as reducing agent. Further trials will be carried out in order to better control the parameters involved in the metallurgical process developed and improve its efficiency.

**Keywords:** biochar; olive stones; reducing agent; metal recovery; waste valorization; pyrometallurgy



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## 1. Introduction

Copper production is a complex process that needs several steps to transform the ore from its mined state into a purified form for use in different industries. In all these steps different waste streams are generated. These wastes have different compositions and, as a first approximation, can be classified into Cu-rich and Cu-poor wastes. In addition to copper, all these wastes also contain valuable metals, and even hazardous elements.

In most of the copper smelting plants, the Cu-rich wastes are usually recirculated as raw material [1]. However, due to the lower concentration of copper in the recirculated wastes, compared to the ore, the yield of the process decreases. Moreover, the repeated recirculation can increase the concentration of hazardous elements downstream. For this reason, efforts have been made to refine the recirculated wastes in order to increase the efficiency of the process. In the case of the Cu-poor wastes, they are commonly considered and handled as wastes in the copper smelting plants, with the associated economic (if sent to an authorized waste manager) and environmental (if landfilled) costs.

One of the main wastes generated in copper smelting plants, which has been studied by several authors, are copper smelting flue dusts. Several treatments have been reported for the refining of these flue dusts, which can be categorized into hydrometallurgical or pyrometallurgical treatments. Regarding the hydrometallurgical treatments, leaching using different reagents (water, acid or alkaline) [2–8] is the most studied process; but a combination of roasting and leaching [9,10] has been also investigated. In the case of pyrometallurgical treatments, a Waelz process followed by a hydrometallurgical process

can be found [11]. According to Moldabayeva et al. [12] the electrothermal combined method, is the most promising and environmentally feasible technology.

The Cu concentration of the copper smelting flue dusts referenced ranges from 1% to 74%. These numbers indicate the high variability in the composition and concentration of the dusts generated. According to Balladares et al. [13] since the composition changes from dust to dust, customized processes must be developed, even if this requires a complex, costly, and difficult to control dust treatment plant, but which is capable of operating as an auxiliary unit of the smelter.

Following this approach, the metallurgical process presented in this paper is a flexible process that can be integrated in the copper smelting plant where the wastes are generated so that they can be treated in-house. In addition, it can be easily adapted to valorize different types of wastes regardless of their composition thanks to the possibility of controlling the temperature on demand, from 300 °C to 2000 °C. It recovers almost 100% of the metallic elements contained in the wastes or by-products, with an efficient energy source, such as high-power thermal plasma (HPTP). This plasma uses electric energy that can be obtained from renewable sources, lowering the GHG emissions, which is one of the main advantages compared to the traditional used Waelz process that uses natural gas. It also enables the possibility of using biochar as a reducing agent instead of fossil fuels, as will be explained in this paper.

In this work metallurgical trials have been carried out with a waste provided by Atlantic Copper, S.L.U. with the aim of showing the possibilities of this technology to valorize Cu-poor wastes. This company has a copper smelting plant located in Huelva (Spain) where more than one million tons of mineral concentrate are transformed into 300,000 tons of refined copper each year [14]. Atlantic Copper is aware of the importance of recycling copper at the end of its useful life as well as any other waste generated in any step of their process to produce copper cathodes. For this reason, the company is increasing the sources of secondary raw materials in their production process in order to recover copper and also any valuable metal it may contain. In 2021, 29,181 tons of recycled copper were processed in the plant, resulting in 8.9% production of new copper from this recycled copper. They are also devoting some efforts to investigate how to improve the quality of the Cu-rich dusts coming from their flash smelting furnace by leaching and at laboratory scale [3]. All these actions are an indicative of the company's commitment to the circular economy.

Despite these efforts, in 2021, 18,617 tons of waste were generated, with 18.2 kg/t being the ratio of waste managed to ore processed [14]. These wastes were recycled and reused through authorized waste managers instead of being disposed of with the associated economical cost for the company. The metallurgical process developed in this work offers the chance to valorize part of these wastes, and do it in-house, thus avoiding its transport to the authorized waste manager, adding the environmental benefits to the economic savings of transforming something that is currently managed as waste into a product.

The interest of these dusts lies in their high content in valuable metals like Pb and Zn. Both metals are interesting in their oxide form because they have several applications. In the metallurgical process developed in this project, these elements are first gasified and secondly re-oxidized in the gas captation system to be finally recovered in a baghouse filter as a dust concentrate. ZnO is used in several sectors, such as ceramics, rubber, or pigments sectors, and PbO can be used also in the glass or ceramics sectors. Usually, such ZnO-rich concentrates are also used by Zn producers as raw material in their processes.

DIGIMET company has previous experience, especially recovering ZnO. The technology developed within the project is a technology covered by two family of patents, i.e., WO2016169780 and EP15382205. This technology has already demonstrated its potentiality to treat electric arc furnace dusts (EAFD) from steelmaking companies. It has been already developed up to TRL7 and it has been adapted to treat dusts with different compositions supplied by companies such as Sidenor, ArcelorMittal and Celsa Group obtaining dust concentrates with ZnO concentrations above 70 wt.%. This process is still under development

to increase its versatility and to be able to treat also metallic wastes from different origins such as those generated in copper smelting processes.

Metallurgical processes, such as the valorization process developed in this work, require a reducing agent to carry out the necessary chemical reactions to recover metallic elements from the compounds of the waste. The most used reducing agents are solid fossil fuels (carbonaceous material), such as coke or anthracite [11,12]. Their combustion contributes to increase the CO<sub>2</sub> emissions. On the road to minimizing the carbon footprint, in this work, a biochar derived from agri-food industry waste has been tested as a reducing agent.

Most of the laboratory research related to the use of biochar in metallurgical applications have been carried out using wood derived pyrolyzed biochars. Solar et al. [15,16] studied the impact of the pyrolysis temperature on the manufacturing of high quality reducing agent materials from woody biomass, in order to reduce the fossil-based CO<sub>2</sub> emissions in the metallurgical processes. Although their results were promising, the main drawback of using forestry-based biomass is its availability. The industrial utilization of this type of biomass could generate another environmental problem (e.g., deforestation) and a strong impact on the ecosystems. Thus, an important advantage of using an agri-food industry waste is the fact that it is an existing waste, which is currently often burned or deposited for disposal in large amounts [17]. When used, it contributes to the circular economy. Pyrolysis is the thermochemical treatment commonly used to produce biochar. This treatment is carried out at temperatures above 500 °C. This implies that, on the one hand, the energy consumption of this process is high, and, on the other hand, the recovery yield is quite low. In this project, torrefaction has been chosen for the thermochemical treatment of the biomass in order to increase the recovery yield of the solid fraction. This means that a higher amount of biochar is obtained when processing the same amount of biomass, and also, to consume a lower amount of energy, thus contributing to a higher sustainability of the whole process unit. Finally, and considering a possible industrialization of the process in the near future, the biomass to be torrefied has been selected according to local availability, valuing proximity and sufficient quantity, economic cost, and safety issues.

In this paper, the feasibility of an alternative metallurgical process to valorize copper smelting flue dusts has been studied. The study preliminarily tested the capacity of recovering valuable elements contained in the waste, as Pb and Zn, and the possibility of achieving this objective with a partial (50%) or even total (100%) replacement of anthracite by biochar as reducing agent, in order to test the potential of this technology to treat this kind of waste.

## 2. Materials and Methods

### 2.1. Raw Materials

#### 2.1.1. Waste

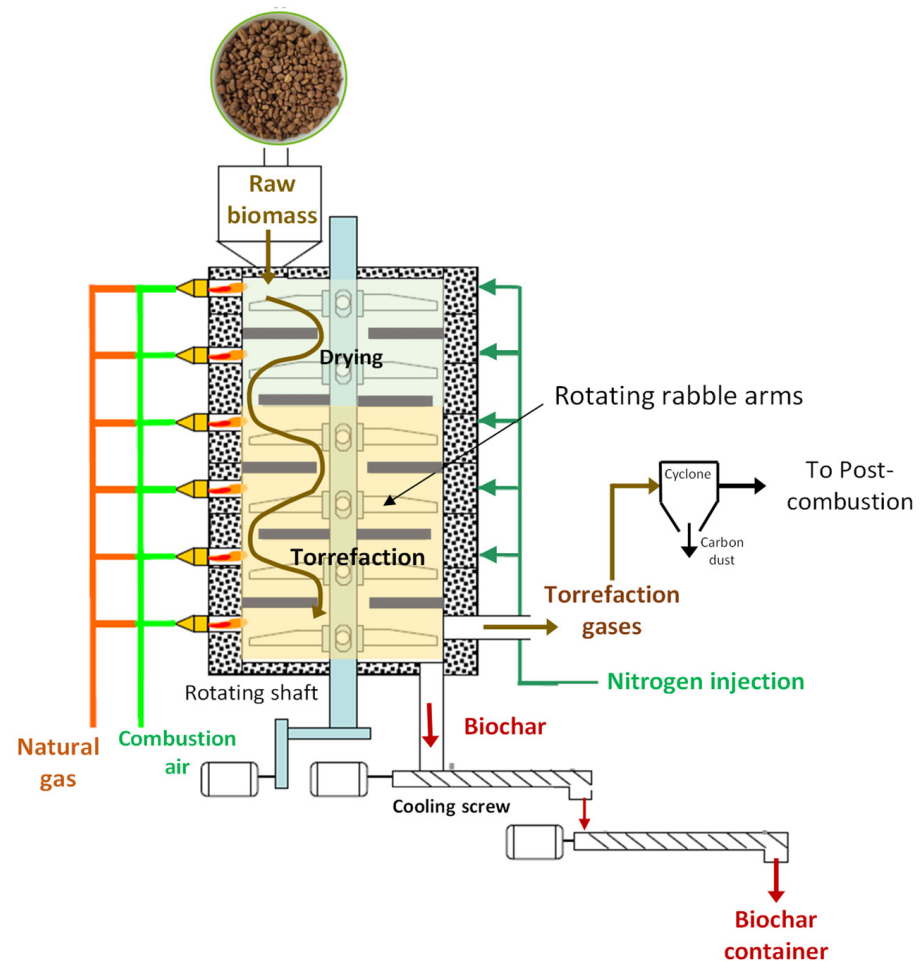
The waste used in this work was provided by the copper smelter of Atlantic Copper, S.A.U. (Huelva, Spain). The waste is the flue dust coming from the electric furnace, where the slags coming from the flash smelting furnace and from the converter are processed.

Two different batches of electric furnace flue dust were supplied by Atlantic Copper to TecNALIA. A sample of some grams of each batch was taken for the chemical and for the metallographic characterization.

#### 2.1.2. Biochar

A torrefied biochar obtained from olive stones at 350 °C was provided by CEA. This material is used as reducing agent in the metallurgical process. It was processed in the multiple-hearth furnace facility of CEA-Grenoble in France (so-called CENTORRE furnace, Figure 1). As explained by Demey et al. [18], two different agricultural residues were studied for their application as reducing agent in the metallurgical industry. The study concluded that both materials had similar values of fixed carbon content and higher heating value (HHV) after being torrefied at 350 °C. However, torrefied olive stones were selected

due to their higher availability and lower cost. A batch was prepared and supplied by CEA for the metallurgical trials.



**Figure 1.** Scheme of the continuous torrefaction pilot plant (multiple-hearth furnace) [18].

### 2.1.3. Anthracite

Anthracite was provided by Tecnia's local supplier Polgraf, S.A. (Lazkao, Gipuzkoa, Spain). This material is used as a reducing agent in the metallurgical process. It has a grain size below 3 mm, and it is usually employed as slag foaming agent in the electric arc furnace (EAF) processes.

### 2.1.4. Bentonite

Bentonite was provided by Tecnia's local supplier HA Ilarduya Group (Amorebieta, Bizkaia, Spain). This material is used as a binder in the preparation of the pellets. It is considered a suitable inorganic material for the agglomeration of different materials with a similar particle size [19].

## 2.2. Preparation of Pellets

Waste and reducing agents (either anthracite, biochar, or a mixture of both) were mixed together with a binder (bentonite) in order to obtain mixtures that could be pelletized to obtain compact pellets.

Both reducing agents, anthracite and biochar, were ground in a rotary ball mill to a particle size of less than 5  $\mu\text{m}$ .

The agglomeration process of the pellets was carried out in a rotary drum mixer. A conventional method with continuous rotation at a speed of 30 rpm was used. The

materials were first dry mixed for 3 min, and then water was added. About 3 L of water are used for 10 kg of waste (0.3 L/kg), and it is slowly added at a rate of 0.3 L/min. The mixing process continued until pellets with enough compactness to be later processed in the furnace were obtained. Even if the objective was to obtain pellets in the range of 5–15 mm, due to the characteristics of the material, there was a fraction with a lower size, but it was considered not critical for the development of the study.

The amount of reducing agent used in the pellets depends on the amount of carbon required to totally reduce the metal oxides present in the waste. However, greater contents than the stoichiometric requirement were added to ensure the total reduction of the oxide metals [12].

Regarding the binder, it was added to the mixture in a content sufficient to obtain a good agglomeration of the waste particles with those of the reducing agent and to obtain, after the pelletizing process, pellets with a good compactness. The content of binder needed is very dependent on the size and the geometry of the waste particles, so a sample of the waste supplied by Atlantic Copper was subjected to scanning electron microscopy (SEM) to be metallographically characterized.

Table 1 shows the concentration of each component in the three different mixtures that were prepared for the metallurgical trials. The first trial was carried out with a mixture containing only anthracite as reducing agent, the second one was carried out with 50 wt.% of anthracite and 50 wt.% of biochar as reducing agent in the mixture, and, finally, the third trial was performed with a mixture containing only biochar.

**Table 1.** Concentration of the components for the different mixtures of pellets (wt.%).

Trial	Waste	Anthracite	Biochar	Binder
1	90.32	4.66	0.00	5.02
2	89.85	2.32	2.73	5.10
3	89.52	0.00	5.42	5.06

### 2.3. Metallurgical Trials

Metallurgical trials were carried out with three different mixtures prepared in the previous step to check the feasibility of the process developed to recover valuable elements from the treated waste when anthracite is partially or totally replaced with biochar.

The process developed in this work is a versatile metallurgical process to valorize different kinds of metal-containing wastes based on the DIGIMET technology. It takes place in a prototype furnace located at TECNALIA's facilities in Irun (Gipuzkoa, Spain), with an almost cylindrical chamber of 600 mm diameter and 600 mm height. It reaches temperatures up to 1450 °C to allow the complex valorization reactions of the oxides contained in the waste, and the gasification of the metallic elements with lower boiling points. The temperature is measured thanks to a thermocouple embedded at the refractory wall next to the furnace chamber, which provides non-direct measurement for continuous power control. Therefore, the furnace heating system must be able to melt and hold materials at temperatures over 1400 °C in continuous operation. To keep these high temperatures, the furnace employs a HPTP system as energy source.

HPTP consists of using a plasma jet that is produced as a result of the ionization of a plasmagen gas between a graphite electrode (the cathode) and the metal bath, which is electrically connected to another electrode (the anode). The plasma is created by generating a potential difference between the two electrodes, causing a chain reaction that ionizes the plasmagen gas to create the plasma arc. Different plasmagen gases can be used, but air has been selected for these trials. Since the metal bath already has the necessary conditions to allow the reduction of the metal oxides, the selected gas does not need to have a specific composition and air has been chosen as a cost-effective alternative. Plasma technology involves the creation of a sustained electrical arc by passing electric current through a gas in a process called electrical breakdown. The current passes through the gas, ionizing it,



and can reach temperatures of over 10,000 °C in the nucleus of the arc [20]. This technology represents a promising trend for the metal waste treatment industry, from the standpoint of energy, materials, and environmental impact reduction when used as a melting system.

The plasma torch used in this furnace has 160 kW of power supply, but an average of 40–65 kW was employed depending on the casting stage. The two electrodes used are made of HP graphite with a diameter of 2.5 inches.

To start with the trials, 130 kg of copper scrap were introduced in the furnace to be heated to above the melting temperature. Once the molten bath was ready and the temperature was stabilized around 1400 °C, the pelletized mixture was added at a feeding rate of 35 kg/h for 2 h (Figure 2). The charging hole is 80 mm in diameter.



**Figure 2.** Feeding of the pelletized mixture to the furnace.

The furnace has a tapping hole, which is also used to directly measure the temperature of the molten metal inside the chamber, when it is needed. During the process, the pellets were dissolved, and the metallic elements contained in the waste were reduced to their elemental form. Some of the elements were dissolved in the copper molten bath, some other were transferred to the slag and those with low boiling points were gasified and left the furnace from the exhaust duct with the exhaust gases. In this duct, they were oxidized again, and finally recovered in the baghouse filter located before the chimney as a dust concentrate.

To determine the mass balance of each element, a sample of the molten metal was taken before and after the addition of the pellets. The chemical composition of each sample was measured. The composition of the slag removed from the surface was also measured and chemical analysis of the dust concentrate was carried out.

#### 2.4. Characterization of the Materials

##### 2.4.1. Proximate and Ultimate Analyses

Samples of anthracite and biochar were ground below 300 µm according to the standard method NF EN 15413. Table 2 summarizes the proximate and ultimate analyses procedures employed.

**Table 2.** Proximate and ultimate analyses procedures.

	Property	Standard Procedure
Proximate analysis	Moisture	Internal method PA 254
	Ash	Internal method PA209 or PA276
	Volatile matter	NF EN ISO 18123
	Fixed Carbon	Calculation/NF M03-006
Ultimate analysis	C, H, N	NF EN ISO 16948
	O	Calculation by difference
	S, Cl	Internal method PA 334

#### 2.4.2. Calorimetric Analysis

A 6200 isoperibol oxygen bomb calorimeter (Parr, Moline-Illinois, IL, USA) was used for determining the HHV of the anthracite and biochar according to the standard method NF EN ISO 18125. The ignition of 1 g of dry sample under oxygen atmosphere was performed at a pressure of 30 bar. Benzoic acid (Merck, Darmstadt, Germany) was used for calibrating the heat capacity of the calorimeter [18].

#### 2.4.3. Chemical Analysis

Two analytical techniques were used to analyze the concentration of the elements in the waste and in the different output streams of the process. Table 3 shows the techniques used for the analysis of each element and the model of the equipment used.

**Table 3.** Equipment used for the chemical characterization.

Sample	Analytical Technique	Analyzed Elements	Equipment Model
Waste	IR detection	C y S	LECO CS-400 automatic analyzer
	Optical Emission Spectroscopy	Rest of elements	ICP-OES spectrometer THERMO model ICAP 7400 DUO
Metallic sample	IR detection	S	LECO CS-400 automatic analyzer
	Optical Emission Spectroscopy	Rest of elements	Spark spectrometer ARL model 3460 UV
	Optical Emission Spectroscopy	As	ICP-OES spectrometer THERMO model ICAP 7400 DUO
Slag	IR detection	C y S	LECO CS-400 automatic analyzer
	Optical Emission Spectroscopy	Rest of elements	ICP-OES spectrometer THERMO model ICAP 7400 DUO
Filter dust	IR detection	C y S	LECO CS-400 automatic analyzer
	Optical Emission Spectroscopy	Rest of elements	ICP-OES spectrometer THERMO model ICAP 7400 DUO

A LECO CS-400 automatic analyzer was used to analyze S and C contents in this work through the infrared detection technique (IR).

The optical emission spectroscopy (OES) technique was used to measure the concentration of the rest of the elements. Two different OES were used depending on the type of sample to be analyzed. For the metallic sample, a spark spectrometer (ARL model 3460) was used to analyze most of the elements, while in the case of the waste, slag, and filter dust, and also the As content in the metallic sample, inductively coupled plasma (ICP) was used. The ICP-OES (Thermo model ICAP 7400 Duo) uses plasma energy as the excitation source.

#### 2.4.4. X-ray Diffraction

X-ray diffraction (XRD) was used to characterize the crystal structure of the waste. In this work the equipment used was the Advance D8 model of Bruker with Cu K $\alpha$  radiation, operated at 40 kV and 30 mA. The diffraction diagrams were measured at the diffraction angle  $2\theta$ , range from  $10^\circ$  to  $90^\circ$  with a step size of  $0.05^\circ$ , and 5 s/step. The powder diffraction file (PDF) database 2008 was applied for phase identification.

#### 2.4.5. Scanning Electron Microscope

The microstructure of the waste was investigated by using SEM, model JEM 5910 LV (JEOL, Croissy-Sur-Seine, France), equipped with an energy-dispersive X-ray analyzer (EDX) to perform a semi-quantitative analysis of the composition of the different phases of the sample.

### 3. Results and Discussion

#### 3.1. Characterization of the Raw Materials

##### 3.1.1. Characterization of Waste

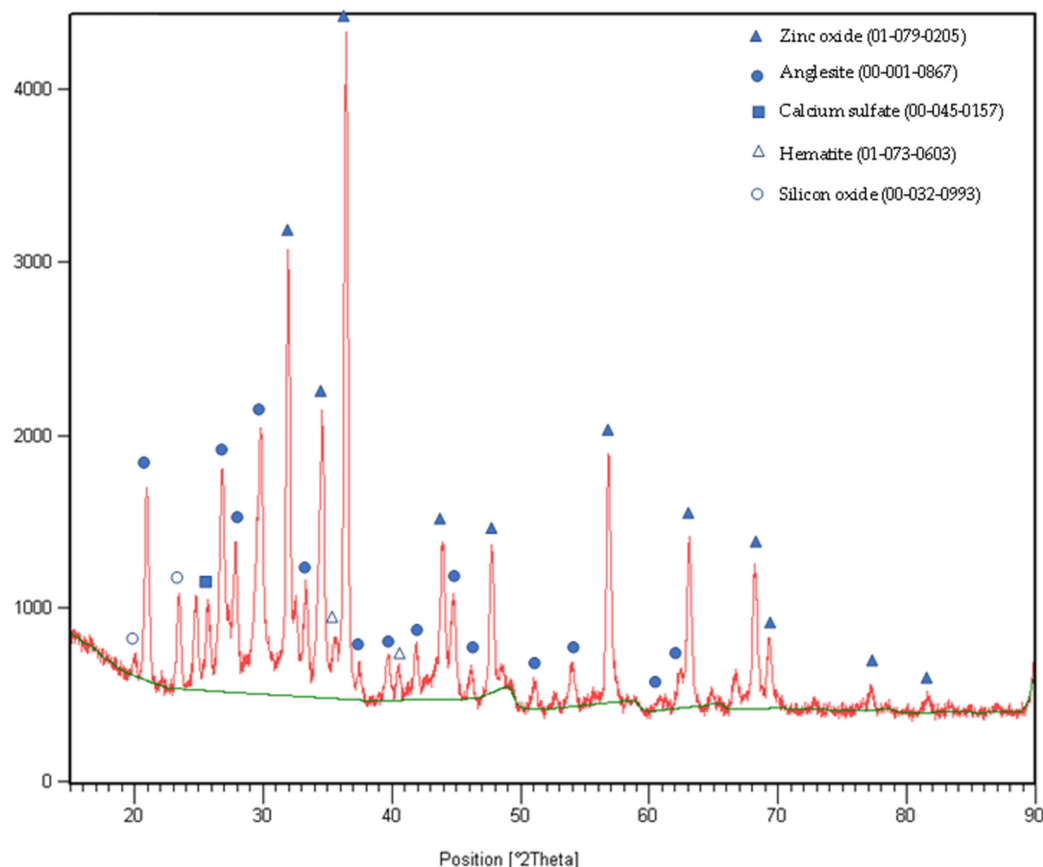
The chemical composition of the two different batches of electric furnace flue dust used in this work is presented in Table 4. The high variability in the concentration of some of the elements can be observed. The composition of this residue is influenced by the stage of the melting process that is occurring in the furnace where it is generated at any given time. This is why the composition of the batches collected at different times is so variable.

**Table 4.** Chemical composition of the two electric furnace flue dust batches (wt.%).

	Zn	Ca	S	Pb	C	Si	Fe	Cu	As	K	Cd	Mg	Mo	Sn
Batch 1	32.40	9.70	4.40	17.50	2.60	1.10	2.10	1.00	0.61	0.22	0.37	0.10	0.21	0.14
Batch 2	10.60	34.52	9.33	2.88	1.90	0.65	0.48	0.44	0.42	0.15	0.10	0.17	0.05	0.05

The variability in the composition is something characteristic of this kind of waste and is one of the reasons that explains the need to develop valorization processes that can be easily adapted to the different types of waste to be processed regardless of their composition.

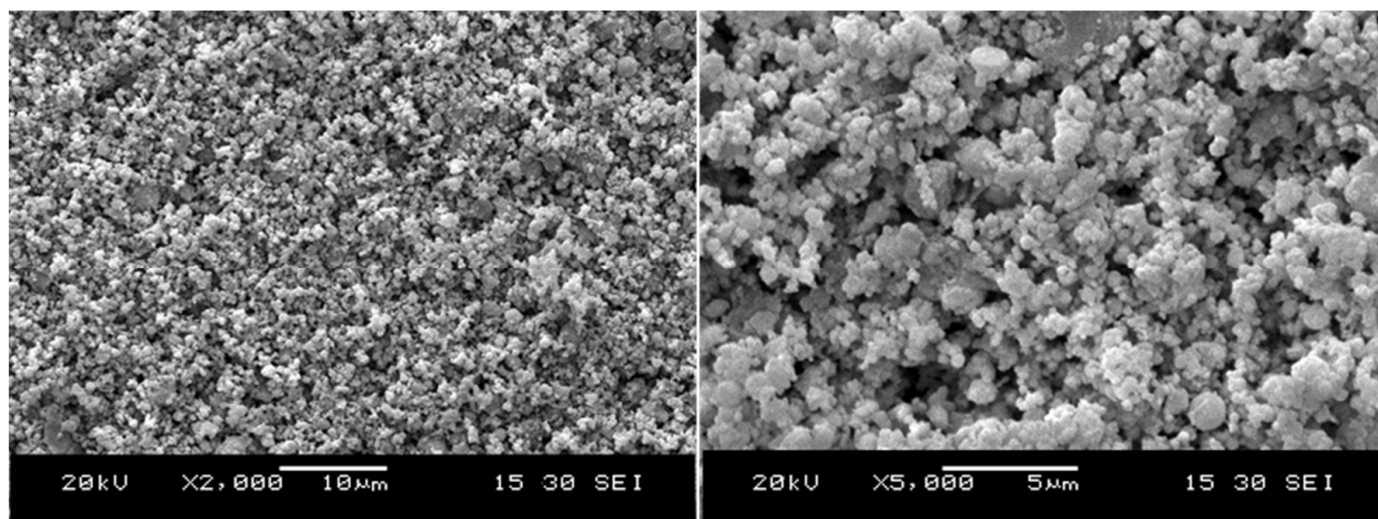
Despite the high variability, the elements with higher concentration in the waste are lead, zinc, calcium and sulfur. They do not appear in their elemental form in the waste but forming simple or even complex compounds. The XRD characterization presented in Figure 3 shows that there are three main compounds in this waste: zinc oxide (ZnO), anglesite (PbSO<sub>4</sub>) and calcium sulphate (CaSO<sub>4</sub>). Moreover, small contents of hematite (Fe<sub>2</sub>O<sub>3</sub>) and silicon oxide (SiO<sub>2</sub>) can be found.



**Figure 3.** XRD pattern of the electric furnace flue dust.



The SEM micrographs in Figure 4 show that this waste is composed by spherical particles with different sizes, but most of them smaller than 5  $\mu\text{m}$ . This was an important parameter to be considered when deciding the average particle size of the reducing agent. Mixtures with similar particle sizes of the different components increase the compactness of the pellets and, consequently, improve their behavior during the metallurgical process.



**Figure 4.** SEM micrographs of the electric furnace flue dust at 2000 magnifications (**left**) and 5000 magnifications (**right**).

### 3.1.2. Characterization of Reducing Agents

The proximate and ultimate analyses in dry basis (db) with the HHV in dry basis of the anthracite and the biochar are presented in Table 5.

**Table 5.** Characterization of anthracite and biochar (wt.% db).

	Property	Anthracite	Biochar [18]
Proximate analysis	Moisture	3.9	<0.1
	Ash	16.4	2.1
	Volatile matter	6.2	31.9
	Fixed Carbon	77.4	66.0
Ultimate analysis	C	81.6	76.3
	H	1.55	4.43
	N	0.82	0.36
	O	<0.2	16.5
	S	1.07	0.015
	Cl	0.02	0.008
HHV (MJ/kg)		28.86	29.84

The carbonaceous materials are interesting as reducing agents due to their content of fixed carbon (FC). When they burn in the furnace, they release carbon dioxide. The generated carbon dioxide reacts in the furnace with carbon to produce carbon monoxide (Boudouard reaction) which is the main reducing agent in the furnace. Consequently, this CO acts as a reducer for the metal oxides, oxidizing itself to CO<sub>2</sub>. In this case, the biochar has 66 wt.% of FC which is slightly lower than the FC content of the anthracite. Since this is the parameter considered to calculate the reducing agent content of the pellets, the higher the content of fixed carbon in the reducing agent, the lower the content of reducing agent needed in the mixture to be able to completely reduce the same content of oxides present in the waste.

A significant difference in the volatile matter (VM) content of both materials can be also observed. Biochar has five times more VM than anthracite. This is because the biochar has been produced at a temperature at which not all the volatiles have been released. Instead, in the case of the anthracite, during the years of formation of this fossil fuel, its VM content has decreased. Since the VM is released at lower temperatures than that at which the FC degrades, considering the higher content of VM of the biochar, the reaction rate of this is usually higher than anthracites. However, both reducing agents in this work have been exposed at very high temperatures (~1300 °C) in a very short time. Therefore, no effect of VM has been observed in the reduction capacity of the reducing agents. Similar results were observed by Konishi et al. [21]. In their study, they show that the reducibility of semi-charcoal pellets was not dependent on the VM content at high temperature (1000 °C), because the reduction temperature was higher than the maximum carbonization temperature to which they had been subjected, and all the VM was released instantaneously when the pellets were introduced into the electrical furnace.

Regarding the ash content, the anthracite has a high content compared to the biochar, but it is a typical value for fossil coals [21–23].

The HHV of both materials are alike and rather high, similar to the HHV of commonly used solid fossil fuels [24]. This indicates that biochar could be valorized (additionally) as a solid fuel for providing energy to the system.

### 3.2. Characterization of the Process Streams

The chemical composition of the different streams has been analyzed to study the distribution of the elements of interest. A sample of the molten metal was taken before and after the addition of the pellets for the purpose of characterization. Analyses of the chemical composition of the slag removed from the surface of the molten bath and that of the dust concentrate were also carried out.

Table 6 presents the chemical composition of the most relevant elements considered in this work. The chemical composition of the raw waste has also been included for comparison.

**Table 6.** Chemical composition of the different streams involved in the metallurgical trials (wt.%).

	Trial 1			Trial 2			Trial 3		
	100% Anthracite			50–50% Anthracite-Biochar			100% Biochar		
	Pb	Zn	Ca	Pb	Zn	Ca	Pb	Zn	Ca
Waste	2.15	7.92	25.79	2.17	7.99	26.02	2.36	8.69	28.16
Metal before	0.86	0.28	-	0.85	0.68	-	0.72	0.28	-
Metal after	0.86	0.69	-	0.74	0.29	-	0.68	0.38	-
Slag	0.05	0.48	43.60	0.15	0.25	36.59	0.05	1.12	29.95
Filter dust	9.19	24.18	0.79	9.28	33.58	2.43	9.75	33.42	2.72

Regarding the elements of interest, such as Pb and Zn, it can be seen in Table 6 that, comparing their initial concentration value in the waste with the concentration in the filter dusts obtained in each trial, they have increased in all of them.

This can be explained by the fact that these two elements are easily gasified under the process conditions used, unlike other elements that are more easily dissolved in the molten bath or transferred to the slag. This is the case of the calcium, which ended up almost entirely in the slag, as it cannot be found in the metal and only in a very low concentration in the filter dust.

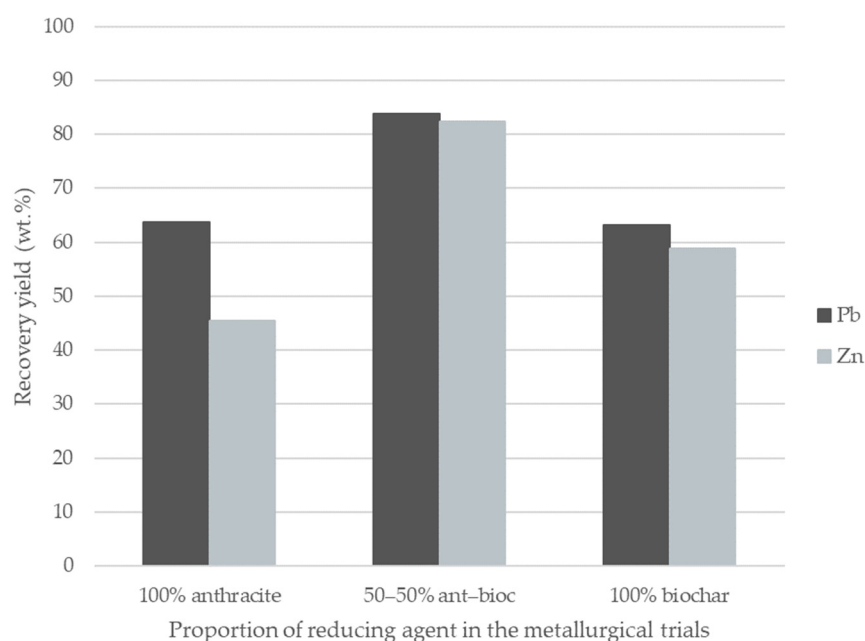
These results show how the objective of reconcentrating the filter dust in the recoverable elements has been achieved.

### 3.2.1. Filter Dusts Recovery Yields

The dust concentrate recovered in the baghouse filter (filter dust) is the main output of the metallurgical process developed in which the electric furnace flue dust is valorized. The feasibility of the developed valorization process has been studied by the recovery yield of specific elements in the filter dusts. For this reason, only the recovery yields of the dusts are presented in this paper.

This work has been focused on the recovery of valuable metals such as Pb and Zn in their oxide form. The recovery yield of these two elements has been calculated, as the percentage of the elements in the waste that is gasified during the valorization process in the furnace and finally recovered in the filter dust.

The recovery yields of the elements of interest in the filter dust for the three trials are depicted in Figure 5.



**Figure 5.** Recovery yields per element in the filter dust (wt.%).

Despite variations on the recovery yields, positive results were obtained with the three pellet mixtures. Pb and Zn passed into a large extent to the filter dust as expected and desired. Recovery yields in the range of 63–84 wt.% for the Pb and in the range of 45–82 wt.% for the Zn were obtained.

Regarding the effect of the reducing agents, no clear conclusions of the influence of replacing anthracite with biochar in the recovery yield of these elements were reached. However, good results were obtained with both reducers. For this reason, the use of biochar seems to be promising in the future as a substitute for current fossil-based reducing agents.

The variations in the recovery yields may be associated with factors, such as the non-homogeneity in the composition of the waste. The values presented in the chemical characterization show that there is a high variability in the composition of the waste. This fact directly affects the furnace process control parameters, causing them to be modified and adjusted as the trials are carried out.

In turn, the variations in the process parameters affect the elements recovery yields. Therefore, it has been found that a better knowledge of the process parameters is necessary so that the trials can be considered representative enough. A way to better control and adjust them is to perform longer-term and higher-volume trials to obtain data and information with more precision and accuracy.

Some of the process parameters that have influenced the metallurgical reactions that take place in the process developed and, consequently, the recovery yields of the different elements are the wear of electrodes and the temperature of the bath.

During the metallurgical trials, the electrodes are consumed. When the wear of the furnace electrodes reaches a determined level, the furnace cannot give enough power. As a consequence, the efficiency of the HPTP is reduced, slowing the metallurgical reactions that take place, thus reducing the recovery yields of the elements.

Another consequence is that the temperature of the melt is slightly cooler, and this affects the fluidity of the slag. Cooler temperatures generate a less fluid slag which prevents a good contact between the molten bath and the pellets, resulting in a greater amount of waste that cannot be introduced into the molten bath and, therefore, is not dissolved.

For this reason, all the factors that have any influence on the temperature of the bath must be identified, controlled, and optimized in order to maintain the slag fluidity under optimal conditions and thus improve the yield of the process.

#### 4. Conclusions

The feasibility of a newly developed metallurgical process has been studied. The capacity of this process powered by an energy efficient HPTP system to valorize flue dust from a copper smelting company has been evaluated. The process has proven able to transform wastes currently managed as residue, with the associated environmental and economic impact, into a by-product with commercial applications.

Recovery yields higher than 60 wt.% for Pb and 45 wt.% for Zn have been obtained in the flue dusts recovered in the baghouse filter, showing that the process is able to enrich the filter dust in valuable metals. Even if the process needs further development to improve the control of the parameters affecting the yield of the process, no significant differences have been observed when replacing anthracite with biochar as reducing agent, showing that the biochar could be a sustainable alternative to reduce fossil-based CO<sub>2</sub> emissions of this kind of process.

In future studies, longer-term and higher-volume metallurgical trials should be performed in order to obtain data and information with greater precision and accuracy, to be able to better control and adjust the process parameters involved to improve the process efficiency.

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