

Article

Leaching of Zinc for Subsequent Recovery by Hydrometallurgical Techniques from Electric Arc Furnace Dusts and Utilisation of the Leaching Process Residues for Ceramic Materials for Construction Purposes

Juan María Terrones-Saeta ^{*}, Jorge Suárez-Macías , Evaristo Rafael Moreno-López and Francisco Antonio Corpas-Iglesias 

Research Group TEP-222 “Materials and Mining Engineering”, Higher Polytechnic School of Linares, Scientific and Technological Campus of Linares, University of Jaen, 23700 Linares, Spain; jsuarez@ujaen.es (J.S.-M.); erm10001@red.ujaen.es (E.R.M.-L.); facorpas@ujaen.es (F.A.C.-I.)

* Correspondence: terrones@ujaen.es



Citation: Terrones-Saeta, J.M.; Suárez-Macías, J.; Moreno-López, E.R.; Corpas-Iglesias, F.A. Leaching of Zinc for Subsequent Recovery by Hydrometallurgical Techniques from Electric Arc Furnace Dusts and Utilisation of the Leaching Process Residues for Ceramic Materials for Construction Purposes. *Metals* **2021**, *11*, 1603. <https://doi.org/10.3390/met11101603>

Academic Editors: Jean François Blais and Anna H. Kaksonen

Received: 22 August 2021

Accepted: 30 September 2021

Published: 9 October 2021

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: Steel is one of the most widely used materials in the past and today. Various techniques are used to recycle this material, including the electric arc furnace. This process has several advantages, but it also has a major disadvantage, namely, the generation of waste such as electric arc furnace dusts. Electric arc furnace dusts are classified as hazardous waste due to their high percentage of heavy metals, including zinc. Consequently, in the present research, the leaching of zinc for recovery with sulfuric acid solutions at ambient temperature and atmospheric pressure is evaluated, as well as the reuse of the leaching process residue as a raw material for ceramic materials. The sulfuric acid solutions were 0.125, 0.25, 0.5, and 1 molar, using clay for ceramic conforming and percentages of the leaching residue from 0–50%. The results showed that the optimum solution was 1 molar sulfuric acid, recovering all the zinc in the sample in 36 h. Furthermore, it was found that the clay-conformed ceramics with less than 40% leaching residue showed acceptable physical and mechanical properties according to standards. Therefore, this research develops a new environmental hydrometallurgy in which metallic elements of interest are valorized and the production of waste is avoided, reducing the deposition of hazardous waste in landfills and the extraction of raw materials for the manufacture of construction materials.

Keywords: hydrometallurgy; metallic elements recovery; mining waste; ceramic; construction materials; circular economy; sustainability

1. Introduction

Steel is a material that was widely used in the past and in the present, as its economy and resistance make it difficult to replace, even today [1]. This material also has the quality of being totally recyclable [2], being able, through different processes, to treat the scrap to obtain a new steel [3]. Among the processes developed for this purpose, the most widely used is the so-called electric arc furnace [4,5].

The electric arc furnace established itself as a process for obtaining steel from scrap due to its simplicity, novelty and optimization [6]. However, it has a series of disadvantages that must also be considered, one of the main ones being the generation of waste [7]. Among these wastes, and due to the fact that the electric arc furnace process is carried out at high temperatures, are electric arc furnace dusts [8]. This waste derives from the capture of particles by means of electrostatic precipitators, baghouses, and cyclones, from the gases produced in the electric arc furnace [9]. The particles retained in the gases reach 99.9% [10], deriving from the most volatile elements found in the scrap, such as zinc. These electric arc furnace dusts are considered by the European Waste Catalogue as a hazardous waste [11], producing about 15–20 kg per ton of final steel [12]. Consequently, it can be stated that

this waste poses a significant environmental problem if it is not properly treated. The main elements of these electric arc furnace dusts are zinc, iron, copper, lead, chromium, manganese, silicon, cadmium, nickel, and calcium [13,14]. Obviously, due to the high temperatures of the electric arc furnace, all of the above elements are in the form of oxides.

Among all the chemical elements mentioned, zinc is the one found in the highest proportion. This chemical element is currently highly valued. So much so that China's consumption in 2000 was 1.4 million tons, exceeding the consumption of the United States, and in 2014 this figure quadrupled, with 6.42 million tons being consumed in China [15]. Therefore, zinc is an element that is currently being revalued, requiring new sources of supply for its procurement and consumption.

Different processes, either pyrometallurgical or hydrometallurgical [16–19], can be used to concentrate and obtain zinc from waste or ores. Hydrometallurgy, based on the leaching of zinc in solutions for its subsequent concentration, has advantages over pyrometallurgical techniques. One of the advantages is that it requires less investment in equipment, has lower energy consumption, is more adaptable to variations in the chemical composition of the raw material being treated, and the efficiency of the process is less dependent on other chemical elements [20]. In addition, leaching of zinc oxides in acidic solutions of relatively low molarity is usually an efficient and fast process. Consequently, the leaching of electric arc furnace dusts by hydrometallurgical methods in acidic solutions at atmospheric pressure and ambient temperature appears to be an attractive solution to the problem of electric arc furnace dust production [21].

However, leaching for hydrometallurgical techniques also has a number of disadvantages. Among them is the production of wastes that can be quite harmful to the environment [22]. Therefore, if environmental hydrometallurgy is desired, not only should zinc be extracted from electric arc furnace dusts, but also the waste from the leaching process should be used as a raw material for new materials. This avoids the extraction of raw materials, avoids the pollution caused by landfill site the leaching residues, and achieves a retention of the polluting elements of the leaching residue in the new material.

In this research, after the zinc leaching process of electric arc furnace dusts in acidic media, the use of the leaching residue in ceramic materials for bricks was proposed. The construction sector is one of the most polluting sectors in existence today [23]. This is mainly due to the fact that large quantities of materials are produced, thus consuming a large amount of raw materials [24]. Furthermore, the ceramic element is capable of retaining, as was corroborated by different authors, the potentially polluting chemical elements of the leaching residue in its ceramic matrix [25,26]. Consequently, ceramic is one of the best materials for the use of the leaching residue without the subsequent production of environmental problems.

In short, in the present research, the electric arc furnace dusts are chemically characterized to evaluate their suitability for leaching, and subsequently, these dusts are leached in sulfuric acid solutions with different molarities and at different times, obtaining the optimum solution and time for the extraction of the highest percentage of zinc. With the leaching residue, different families of ceramics are conformed and the physical and mechanical properties of these families are evaluated. In this way, a ceramic is obtained that retains the leaching of polluting elements from the leaching residue. This research is therefore based on the new circular economy, since the elements of interest are extracted from a waste produced by the industry and the leaching residue is reused for new ceramic materials, creating a process in which the waste is null and reduces the environment affection.

2. Materials and Methods

This section describes the main materials used in this research, as well as the tests carried out to obtain a clear and scientific methodology to assess the possible leaching of zinc from electric arc furnace dusts and its subsequent use in ceramics.

2.1. Materials

The materials used in this research are mainly electric arc furnace dusts, distilled water and sulfuric acid for zinc leaching, as well as clay for conforming ceramics with the leaching residue. These materials are described in detail below.

2.1.1. Electric Arc Furnace Dust

The steel dust used in this research, as mentioned above, corresponds to the material that is deposited in the fume filtering installations during the melting process in the electric arc furnace, and the sample of this waste was taken directly from the producing steel company located in Andalucía, Spain.

The electric arc furnace dust samples were taken in a representative manner according to the regulations, sampling for months to verify that the physical and chemical characteristics of the waste did not vary over time with different production batches.

The samples after collection were dried at a temperature of 105 ± 5 °C to remove any humidity they might contain. In this way, unnecessary variables that could cloud the results of the tests mentioned in the methodology were avoided. Due to the small grading of the electric arc furnace dusts, this material was used directly for the characterization and leaching tests, without any intermediate milling process.

2.1.2. Sulfuric Acid and Water

The sulfuric acid used in this investigation has a purity of 96%, with a molar mass of 98.08 g/mol. This acid was diluted with different concentrations of distilled water to obtain sulfuric acid solutions of different molarities. In this way, it was possible to study the concentration of zinc produced with different acid solutions at atmospheric pressure and in different periods of time. The distilled water used has a colorless liquid appearance, a density at 20 °C of 0.995 g/cm³, a pH of 7, a conductivity in $\mu\text{S}/\text{cm}$ of 2.5, a silica percentage of 0.003 mg/L, and a hardness measured in mg/L CaCO₃ of 0.3.

2.1.3. Clay

The waste obtained after the leaching process of the electric arc furnace dusts was used as an additive or raw material for the production of brick ceramics. Consequently, the use of clay is necessary for the conforming of the different families of ceramics.

The clay used corresponds to that extracted in the province of Jaén, Spain. This type of red clay was used for decades for the manufacture of bricks for construction, and there are currently several production industries in the area that produce and market this material.

The red clay used has a very small particle size, similar to electric arc furnace dust. This clay was dried at a temperature of 105 ± 5 °C, as were the steel dust, for its subsequent characterization and use in ceramics. No milling process was carried out on the clay, but the sample of this material was sieved through a 0.25 mm sieve.

2.2. Methodology

The methodology followed in this research is based on a series of logically ordered tests to verify the main objective of this research, leaching zinc from electric arc furnace dusts with sulfuric acid solutions at ambient temperature and atmospheric pressure, as well as reusing the leaching residue for the shaping of ceramics that avoid environmental pollution from the leaching process waste.

To do this, first of all, the electric arc furnace dusts were chemically characterized. In this way, it was possible to identify the percentage of zinc in the sample, as well as the existence of other elements hazardous to the leaching process. Subsequently, the leaching process was carried out with different sulfuric acid solutions, measuring the fundamental leaching parameters every 24 h. The results obtained were used to select the optimum solution and leaching times for the recovery of the highest percentage of zinc, and the leaching residue was chemically analyzed after filtering. With the leaching residue, different families of ceramics with different percentages of waste and clay were

conformed. These ceramics were physically and mechanically characterized, determining the maximum percentage of incorporation of the leaching residue in ceramics.

In the following sections, the tests corresponding to each phase of this research are detailed in more detail.

2.2.1. Chemical Characterization of Electric Arc Furnace Dusts

The electric arc furnace dusts after drying were chemically characterized to determine the percentage of zinc in them, as well as to evaluate the existence of certain chemical elements that could impair the leaching process.

For the chemical characterization, the first of the tests carried out was elemental analysis, detecting the percentage of carbon, hydrogen, nitrogen, and sulfur in the sample. This test was performed with LECO's TruSpec Micro (TruSpec Micro, LECO, St. Joseph, MI, USA).

Subsequently, the loss-on-ignition test of the electric arc furnace dusts was carried out at a temperature of 950 ± 5 °C. Therefore, this test quantifies the existence of organic matter, the existence of carbonates, the existence of volatile elements, and even the transformation of certain chemical compounds.

Finally, to identify and quantify the chemical elements with the highest atomic weight, the X-ray fluorescence test was carried out. This test was performed with the ADVANT'XP+ commercial equipment (ADVANT'XP+, Thermo Fisher, Waltham, MA, USA).

2.2.2. Leaching of Electric Arc Furnace Dusts in Sulfuric Acid Solutions at Ambient Temperature and Atmospheric Pressure

For the recovery of the zinc present in the electric arc furnace dusts, leaching was carried out in acidic media, at atmospheric pressure, ambient temperature (25 ± 1 °C), and in immersion with constant agitation. This leaching system was selected because it is the most suitable for the waste, since electric arc furnace dusts have a small particle size and a high percentage of zinc.

The process consists of leaching the zinc present in the sample, which is in the form of ZnO and ZnFe₂O₄, using different H₂SO₄ sulfuric acid solutions with different molarities. The selected molarities of sulfuric acid were 0.125, 0.25, 0.5, and 1 molar. These molarities were selected for different reasons; on the one hand, it was not desirable to use high molarities of sulfuric acid to not create a highly toxic leaching residue; on the other hand, the chemical adjustment determined that these molarities were sufficient to leach the existing zinc in the sample, and finally, it was intended to reduce the environmental impact of the process that would occur if high molarities of sulfuric acids were used.

The sample of electric arc furnace dusts was 5000 ± 5 milligrams. This sample was mixed in 100 ± 1 mL of the corresponding solution and stirred for the 5 days of the test. The pH was measured every 24 h and the electrical conductivity of the solution was determined. In addition, a sample of 5 mL was taken every 24 h for analysis by inductively coupled plasma mass spectrometry (7900, Agilent, Santa Clara, CA, USA). In this way, the variation of the zinc concentration in the leachate could be obtained, as well as the modification of the pH and conductivity of the solution.

The results of the zinc concentration in the leachate made it possible to determine the sulfuric acid solution that produced the greatest recovery of the zinc in the sample, as well as the time in which this recovery occurred. Therefore, the optimum dilution and time to recover the zinc in the electric arc furnace dusts was determined.

2.2.3. Chemical Characterization of the Leaching Residue

Once the optimum sulfuric acid solution was selected that produced the highest zinc recovery in the optimum time, large quantities of electric arc furnace dust were leached under the detailed conditions of solid/liquid, temperature, times, etc.

The leaching residue were filtered with filter paper, obtaining a solid waste that was subsequently dried at a temperature of 105 ± 5 °C for 24 h. This leaching residue was

chemically characterized to determine its hazardousness, as well as the chemical elements that could be detrimental to the ceramic conformed with them.

The chemical characterization of the waste was similar to that carried out for electric arc furnace dusts. Consequently, the elemental analysis test was carried out to determine the percentage of carbon, nitrogen, hydrogen, and sulfur in the sample with LECO's TruSpec Micro commercial equipment (TruSpec Micro, LECO, St. Joseph, MI, USA). Subsequently, the loss on ignition test was performed at 950 ± 5 °C, and the X-ray fluorescence test, to quantify the elements of higher atomic weight in the leaching residue, with the ADVANT'XP+ commercial equipment (ADVANT'XP+, Thermo Fisher, Waltham, MA, USA).

2.2.4. Conformed of Ceramic Materials for Bricks with the Leaching Residue of Electric Arc Furnace Dusts

Once the leaching residue was analyzed, different families of ceramics with different percentages of clay and waste were conformed. The initial family was composed only of clay, therefore, the ceramic formed was a conventional material. This family was made to compare the physical and mechanical properties of the ceramics conformed with the leaching residue. Subsequent families were formed with increasing percentages of 10% leaching residue. Table 1 shows the various families of ceramics evaluated, as well as the percentage of clay and leaching residue for each.

Table 1. Families of ceramic samples conformed with clay and leaching residue.

Ceramic Family	% of Clay	% of Leaching Residue
RL0	100	0
RL1	90	10
RL2	80	20
RL3	70	30
RL4	60	40
RL5	50	50

For the production of the detailed ceramic samples, the dry mass of clay and leaching residue was mixed according to the family. Once the mixture was homogenized, 10% water was added to facilitate the mixing of the mixture and allow for better compaction. The detailed mixture was poured into a metal matrix of dimensions 60×30 mm, subsequently applying a compression pressure of 25 MPa. The use of this percentage of water and the detailed pressure was selected because of the similarity of results between the material conformed in the laboratory and that obtained in industry. Finally, the sample was extracted and dried at a temperature of 105 ± 5 °C for 24 h. A total of 6 samples were made for each family to obtain statistically reliable results.

A sintering process is essential for the shaping of ceramics. In this research, the sintering process consisted of raising the temperature of the dried specimens to 950 ± 5 °C, using a temperature ramp of 4 °C/min. The samples of all the families conformed according to the detailed procedure were subjected to the physical and mechanical tests detailed below to evaluate their quality.

The first physical tests carried out were the determination of the linear shrinkage and the mass loss that occurs in the ceramic before and after the sintering process. Subsequently, capillary water absorption (UNE-EN 772-11 standard), cold water absorption (UNE-EN 772-21 standard), and determination of open porosity and bulk density (UNE-EN 772-4) tests were carried out.

Once the physical properties were determined, the mechanical strength of the different families of samples was evaluated. The compressive strength test was carried out for each of the specimens of each family according to the UNE-EN 772-1 standard. This test is

essential, since the element for which the ceramic material is intended is for bricks and must have a compressive strength greater than 10 MPa according to the standard.

3. Results and Discussions

3.1. Chemical Characterization of Electric Arc Furnace Dusts

The first of the tests carried out for the chemical characterization of the electric furnace steel dust was the elemental analysis test. The elemental analysis test shows that the percentage of nitrogen (0.027 ± 0.001) and sulfur (0.101 ± 0.003) in the sample is quite low. Consequently, it is corroborated that the chemical composition of the electric furnace dusts is mainly composed of oxides, and that there are no more volatile elements such as nitrogen that could complicate the leaching process. At the same time, the low percentage of carbon (2.053 ± 0.048) and hydrogen (0.270 ± 0.009) shows that the dusts have practically no percentage of organic matter. On the other hand, the carbon in the sample can be derived directly from the carbonation of the oxides, as well as the percentage of hydrogen from the hydration of certain compounds.

The loss on ignition test of the electric arc furnace dusts showed a value of $14.87 \pm 0.348\%$. This variation in mass before and after subjecting the sample to the temperature of 950 ± 5 °C may be due to the existing organic matter, carbonates, hydration of certain compounds, and even the transformation of certain chemical compounds. In this case, and on the basis of the results obtained in the other chemical tests, it could be affirmed that this mass variation corresponds to the carbon in the carbonate compounds and other volatile elements, as well as the transformation of certain chemical compounds.

The X-ray fluorescence test of the electric arc furnace dusts showed the results detailed in Table 2.

Table 2. X-ray fluorescence of electric arc furnace dusts.

Element	Wt %	Est. Error
Fe	23.12	0.16
Zn	18.83	0.17
Ca	4.78	0.09
Si	2.06	0.05
Cl	3.93	0.10
Na	2.52	0.15
Mg	1.66	0.05
K	1.42	0.05
Mn	1.18	0.05
Al	0.752	0.03
Pb	0.805	0.040
Sx	0.329	0.016
Cr	0.186	0.0093
Cu	0.194	0.0097
Px	0.0766	0.0038
Ti	0.0656	0.0033
Cd	0.0646	0.0032
Sn	0.0512	0.0061
Ni	0.0267	0.0014
W	0.0259	0.0078
Pt	0.0204	0.0059
Pd	0.0181	0.0026
Co	0.0143	0.0021
Zr	0.0135	0.0023
Ru	0.0100	0.0014
Ag	0.0104	0.0029

As can be seen, the chemical element with the highest percentage in the sample is iron, which is to be expected if we take into account that this waste comes from the filtering of gases from the electric arc furnace fed with ferrous scrap. In turn, zinc makes up a

very high percentage of the electric furnace dust, and it is this zinc in the form of oxide that is to be recovered in this research through leachates. The other chemical elements calcium, silicon, chlorine, sodium, magnesium, potassium, and manganese are found in much smaller proportions, all of them being common in the waste produced in the iron and steel industry, as they are common elements found in the scrap used as raw material. The remaining chemical elements are found in much smaller proportions, and in principle, do not pose a problem for the leaching process.

3.2. Leaching of Electric Arc Furnace Dusts in Sulfuric Acid Solutions at Ambient Temperature and Atmospheric Pressure

The characterized electric arc furnace dust was subjected to the leaching process detailed in the methodology with 0.125, 0.25, 0.5, and 1 molar sulfuric acid solutions. This leaching process, carried out with a 1:20 solid/liquid ratio and with continuous agitation at 500 rpm, was evaluated to corroborate the extraction of zinc from the sample of electric arc furnace dusts. To evaluate the process, the pH, electrical conductivity and zinc concentration of the solution were measured every 24 h. These measurements, always carried out at a temperature of 25 °C, are detailed below.

The variation of the pH for the different leaching solutions at different times and according to the detailed process are shown in Figure 1.

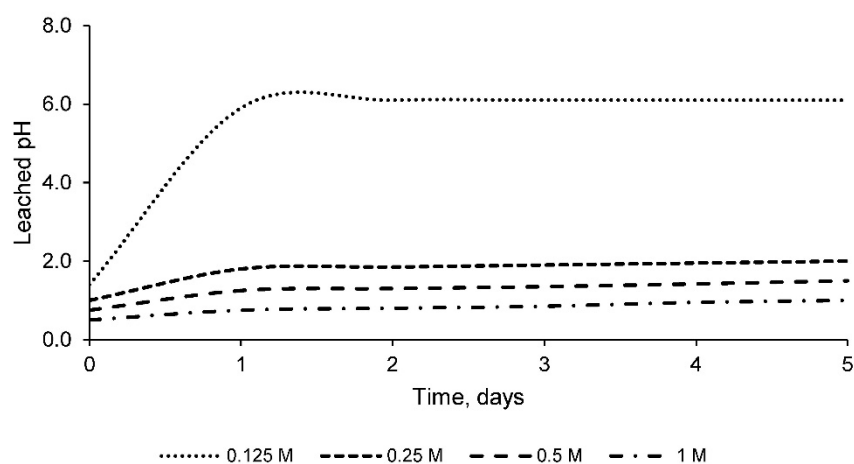


Figure 1. pH of 0.125, 0.25, 1, and 2 molar solutions of sulfuric acid at different times during leaching process with electric furnace dusts.

Figure 1 shows how the 0.125 molar solution of sulfuric acid undergoes a rapid rise in pH in the first 24 h, stabilizing at a pH of 6 over the time evaluated. This elevation of pH is obviously due to the mixing of the acidic solution with the basic electric arc furnace dust sample. Consequently, after 24 h, no further leaching of any chemical element will occur, as the solution is practically neutralized. Therefore, the leaching of the chemical elements from the electric arc furnace dusts that occurred in the 24 h is almost constant.

Something similar happens in the 0.25 molar solution, since in the first 24 h there is a considerable elevation of the pH and after this period of time the value stabilizes. However, in the 0.5 and 1 molar solutions of sulfuric acid, a different situation occurs according to the results shown in Figure 1. On the one hand, and just like the 0.125 molar and 0.25 molar solutions, the most drastic increase in pH occurs in the first 24 h. However, over the course of the days, the pH continues to rise progressively much less rapidly. Therefore, it can be estimated that there is still a process of leaching of the chemical elements from the sample of the electric furnace dusts in the following days, in contrast to the 0.125 molar solution which is saturated 24 h into the process.

In turn, the results of the electrical conductivity for the 4 sulfuric acid solutions (0.125, 0.25, 0.5, and 1 molar) are shown in Figure 2 for different times, measured at a temperature of 25 °C.

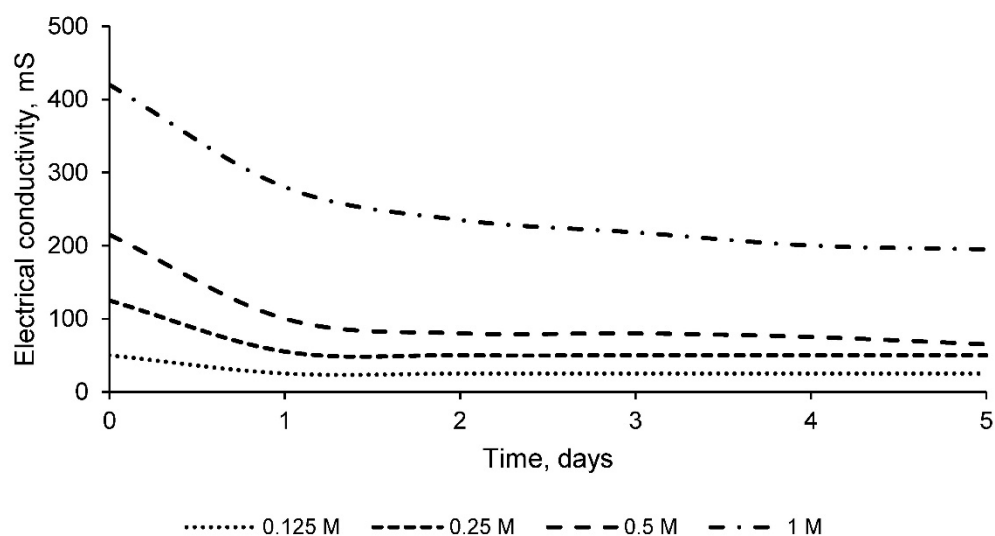


Figure 2. Electrical conductivity of 0.125, 0.25, 1, and 2 molar solutions of sulfuric acid at different times during leaching process with electric furnace dusts.

The results shown in Figure 2 of the electrical conductivity of the solution during the leaching process reflect similar conclusions to Figure 1 in relation to pH. Initially, the sulfuric acid solutions with a higher molarity have a higher electrical conductivity due to the existence of a higher percentage of free ions. The 0.125 and 0.25 molar solutions of sulfuric acid show a significant decrease in conductivity in the first 24 h, obtaining a value that is practically maintained over time. On the other hand, the 0.5 and 1 molar sulfuric acid solutions show a significant decrease in conductivity in the first 24 h but continue to experience a decrease in electrical conductivity during the test time. This shows that chemical elements continue to leach from the sample throughout the test time. However, the interesting element to obtain in the present investigation is zinc. Consequently, if a significant recovery occurred in the first hours, maintaining the time of the leaching process for longer is counterproductive, since other chemical elements are being leached that are of no interest and that also harm the subsequent process of obtaining the zinc by hydrometallurgy of the leachate.

Therefore, the determination of the zinc recovery rate in the different sulfuric acid solutions and at different times will establish which is the appropriate leaching time to obtain zinc, as well as the solution that provides a greater recovery of zinc from the electric arc furnace dusts. The results of this test carried out with the equipment detailed in the methodology are shown in Figure 3.

In Figure 3, the 0.125 molar sulfuric acid solution achieves a zinc recovery rate of over 30% during the first 24 h, with this ratio stabilizing over time. This fact reflects that the aforementioned solution is not capable of leaching a higher percentage of zinc, since it is almost neutralized in the first 24 h, as shown by the pH and electrical conductivity values. On the other hand, the 0.25 molar sulfuric acid solution experiences a rapid increase in zinc recovery rate in the first 24 h and later a much slower increase thereafter, since, as observed in the pH test, this solution after 24 h it remains acidic and still has the potential for zinc recovery. However, for the recovery of zinc with this solution in a viable percentage, a long time would be needed, which would make the process economically unfeasible.

The 0.5 and 1 molar solutions allow a complete recovery of the zinc in the electric arc furnace dusts. The 0.5 molar solution leaches the zinc from the sample after approximately 72 h, so this would be the test time for the recovery of the element. In turn, the 1 molar sulfuric acid solution allows complete leaching of the zinc in a time between 24 and 48 h, approximately 36 h. Consequently, and due to the fact that this process of constant agitation of the sample immersed in the solution has a higher economic cost than other hydrometallurgical processes and, therefore, it is used in samples with a high percentage of

zinc and in reduced times of days, the optimum solution is the 1 molar solution of sulfuric acid with a leaching time of 36 h. Longer times would mean an absurd higher economic cost, as other chemical elements of no economic interest would be leached and could even harm the subsequent hydrometallurgical process.

To quantify the concentration of zinc, as well as the chemical elements potentially unfavorable for subsequent hydrometallurgical techniques, Table 3 is presented. Table 3 shows the concentration in the leachate of the chemical elements mentioned for the aforementioned solution and for the determined test time.

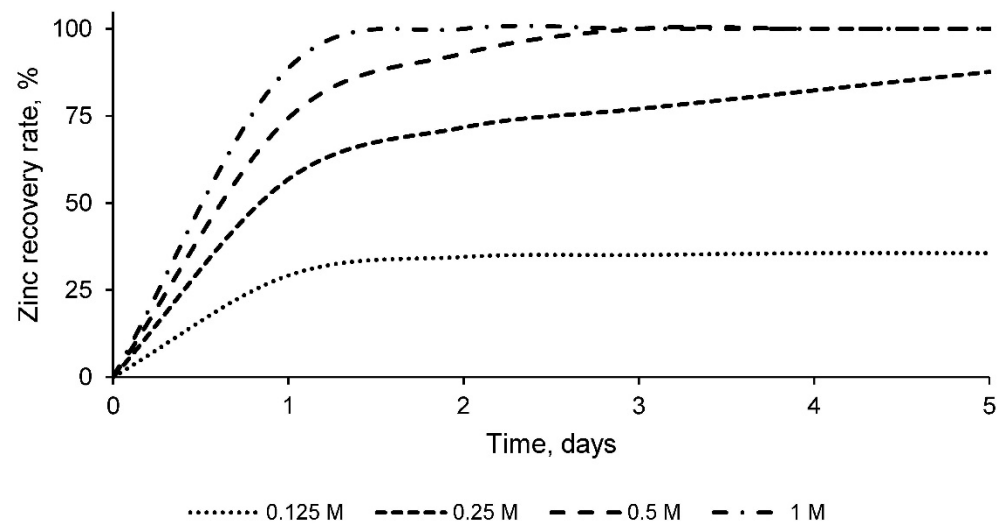


Figure 3. Zinc recovery rate of 0.125, 0.25, 0.5, and 1 molar solutions of sulfuric acid at different times during leaching process with electric furnace dusts.

Table 3. Concentration in leachate of zinc and chemical elements potentially detrimental to development of hydrometallurgical techniques in a 1 molar sulfuric acid solution and a leaching time of 36 h.

Chemical Element	Concentration in Leachate, mg/g
Fe	96.4 ± 1.1
Zn	189.7 ± 3.0
Ca	13.3 ± 0.2
Al	3.7 ± 0.0
Mn	7.9 ± 0.1
Mg	13.1 ± 0.2

As can be seen in Table 3, the concentration of zinc in the leachate, for the selected sulfuric acid solution and the determined test time, coincides with a complete recovery rate. At the same time, the concentration of iron in the leachate is not total, so this fact corroborates that the selected leaching time is adequate, as it recovers a very high percentage of zinc and avoids the leaching of other harmful elements such as iron. The rest of the chemical elements, which can be detrimental to the correct performance of subsequent zinc extraction techniques, are found in very low concentrations.

3.3. Chemical Characterization of the Leaching Residue

The solution of 1 molar sulfuric acid was selected for the leaching of the zinc existing in the electric arc furnace dusts during a test time of 36 h. Therefore, the electric arc furnace dust was leached with this solution and with the detailed time, the solution was subsequently filtered and a leaching residue was obtained. This leaching residue contains, as mentioned above, a series of chemical elements that are very negative for the environment and must be evaluated.

The first of the chemical tests carried out was the elemental analysis test, performed on the leaching residue, which was filtered and then dried at a temperature of 105 ± 5 °C for 24 h. The results of this test are shown in Table 4.

Table 4. Results of elemental analysis of leaching residue.

Sample	Nitrogen, %	Carbon, %	Hydrogen, %	Sulphur, %
Leaching residue	0.024 ± 0.001	0.053 ± 0.001	5.451 ± 0.177	3.745 ± 0.088

The elemental analysis test of the leach residue, shown in Table 4, shows that the percentage of nitrogen is similar to that obtained in the elemental analysis test of the electric arc furnace dusts. At the same time, the percentage of carbon was considerably reduced in the leaching residue compared to that of the electric arc furnace dusts, existing a much higher percentage of hydrogen and sulfur in the leaching residue. This higher percentage of hydrogen and sulfur derives largely from the 1 molar sulfuric acid solution with which the sample was in contact.

In turn, the loss on ignition test of the leaching residue determined a value of $7.57 \pm 0.27\%$. This percentage of mass variation before and after the sample was subjected to the temperature of 950 ± 5 °C corresponds with high probability to the loss of volatile elements and to the transformation of certain chemical compounds. However, the X-ray fluorescence test provides the most information on the chemical elements of higher atomic weight in the leaching residue. The results of this test for the leaching residue are shown in Table 5.

Table 5. X-ray fluorescence of leaching residue.

Element	Wt %	Est. Error
Fe	28.85	0.17
Ca	8.26	0.11
Sx	4.53	0.06
Si	2.12	0.05
Pb	2.01	0.07
Al	1.01	0.04
Mg	1.12	0.04
Mn	1.31	0.05
Zn	0.84	0.02
Cr	0.267	0.013
Cu	0.148	0.0074
K	0.122	0.0061
Ba	0.119	0.040
Ti	0.0759	0.0038
Cl	0.123	0.0062
Sn	0.0795	0.0067
Ni	0.0367	0.0018
Px	0.0195	0.0025
Zr	0.0262	0.0031
Co	0.0206	0.0025
Sr	0.0189	0.0024
Ru	0.0091	0.0019
Bi	0.0107	0.0040
Mo	0.0068	0.0015

The X-ray fluorescence test shows that the percentage of zinc decreased considerably in the sample, thus confirming that a correct zinc leaching process took place for subsequent hydrometallurgical processes. The leaching residue shows a high percentage of iron, which was initially present in the electric furnace dusts and which was not fully leached out. This is interesting, as iron leaching is not as economically interesting as zinc leaching and also

impairs the concentration process. The same applies to the chemical elements calcium, silicon, lead, aluminum, magnesium, and manganese, which were present in the initial sample of electric arc furnace dusts and are still present in the leaching residue, and were therefore not fully leached out in the detailed leaching process with the 1 molar solution. The existing the percentage of sulfur derived from the sulfuric acid leaching process which was not present in such a high proportion in the initial sample of electric arc furnace dust. Consequently, the leaching residue after leaching of the zinc in the sample presents certain potentially polluting chemical elements that must be treated or incorporated into a new material to avoid its deposition in landfill and possible environmental problems. The potentially toxic elements determined by the EPA for ceramic materials are Cr, Pb, As, Cd, and Ba, being these elements the ones that should be evaluated with leaching tests (TCLP) in the material that incorporates this leaching residue.

3.4. Conformed of Ceramic Materials for Bricks with the Leaching Residue of Electric Arc Furnace Dusts

The electric arc furnace dusts were leached in large quantities with a 1 molar solution of sulfuric acid for 36 h and to be subsequently filtered to obtain a sufficient amount of leaching residue for ceramics conforming. The conforming ceramics families are detailed in Table 1, and a total of 6 samples were made for each group according to the procedure detailed in the methodology. These samples, with up to 50% of the leaching residue, were physically and mechanically evaluated through different tests.

The first of the tests performed was the linear shrinkage test, which determined the variation in dimensions that occurred in the samples before and after the sintering process. The results of this test for the different families of ceramics conformed with the leaching residue are shown in Figure 4.

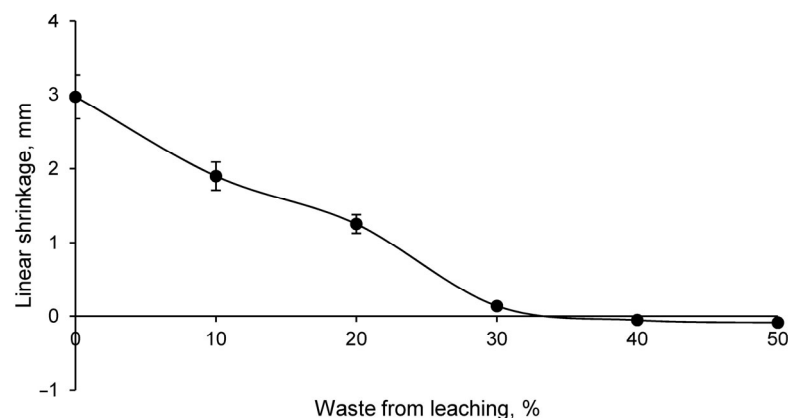


Figure 4. Linear shrinkage of different families of conformed ceramics with clay and leaching residue.

The linear shrinkage of the families of ceramics conformed with the leaching residue decreases with increasing percentage of the waste. So much so that the samples with 40% and 50% leaching residue show an expansion after the leaching process. These results are essential for the industrialization of the ceramic with the leaching residue, since the conformed ceramic must have certain dimensions. To be marketed, so that the dimensions of the material before sintering must be fixed. In addition, a linear expansion reflects an increase in the size of the material and, consequently, the formation of a more open structure, conditioning porosity, density, and even strength.

On the other hand, the weight loss experienced by the conformed ceramic material with various percentages of leaching residue before and after the leaching process is shown in Figure 5.

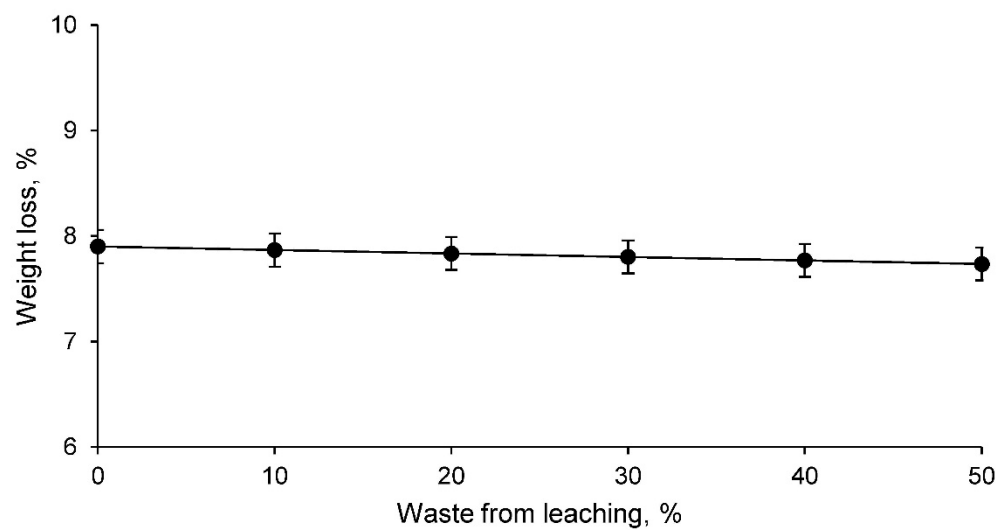


Figure 5. Weight loss of different families of conformed ceramics with clay and leaching residue.

The weight loss in the different families is linear, which is to be expected if one takes into account that the percentage of waste increases in increments of 10%. The result for the clay-only family coincides approximately with the value of loss on ignition of the clay, so that the addition of percentages of leaching residue makes this value vary proportionally based on the loss by calcination of the waste. The weight loss of ceramic families with higher percentages of leaching residue is higher. Consequently, if there is a higher weight loss and a linear expansion, a more open ceramic structure is obviously being created.

This fact can be verified with the capillary water absorption test of the different ceramic families shown in Figure 6.

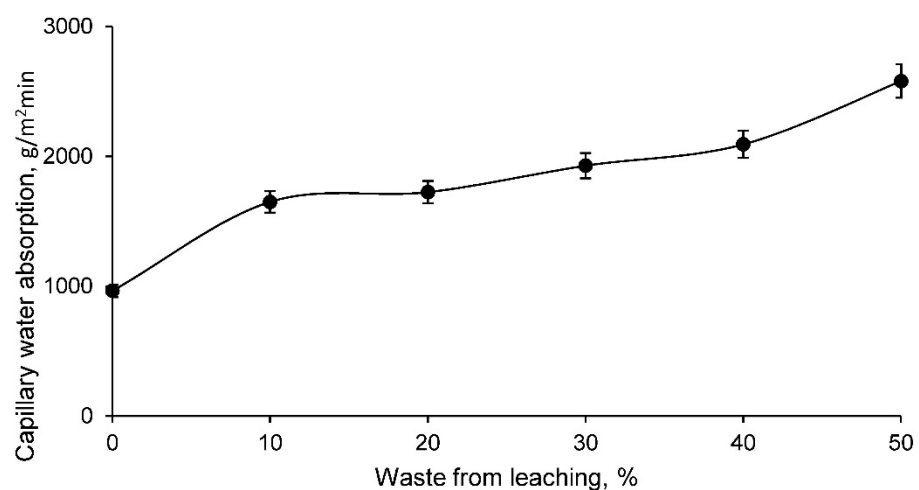


Figure 6. Capillary water absorption of different families of clay-conformed ceramics and leaching residue.

As expected from the results of linear shrinkage and weight loss, the capillary water absorption of the clay-conformed ceramics families and the leaching residue is higher the higher the percentage of waste. Consequently, there is a more open structure in the ceramics with leaching residue, in which there is a series of interconnected pores capable of absorbing a higher percentage of water by capillary action.

The cold water absorption test of the conformed ceramics shows the results shown in Figure 7.

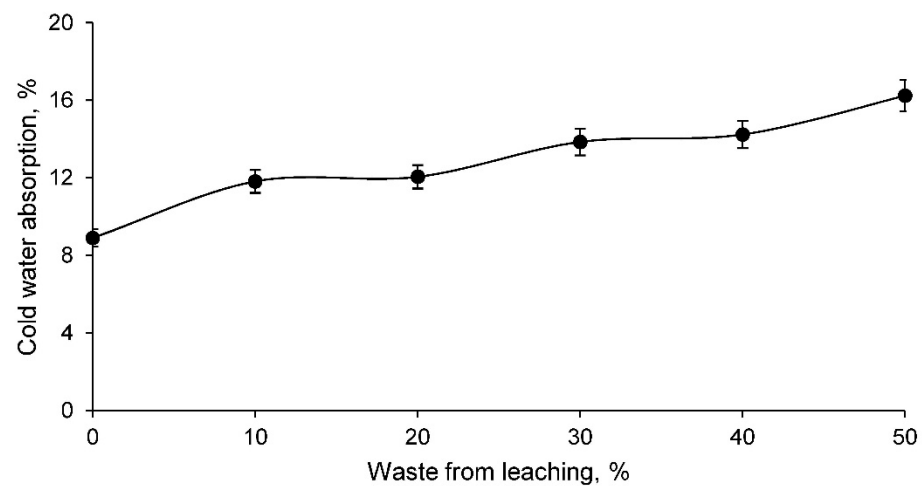


Figure 7. Cold water absorption of different families of clay-conformed ceramics and leaching residue.

The cold water absorption of the conformed ceramic families increases as the percentage of leaching residue in the ceramic increases. This fact is very interesting and must be controlled for ceramic elements that are outdoors, since rainwater can cause it to be absorbed by the ceramic and increase its weight, uselessly overloading the structure that supports these materials. However, a higher water absorption also presents some special characteristics for ceramics that are very interesting for construction.

In turn, the results of the open porosity test for all families of clay-conformed ceramics with leaching residue are shown in Figure 8.

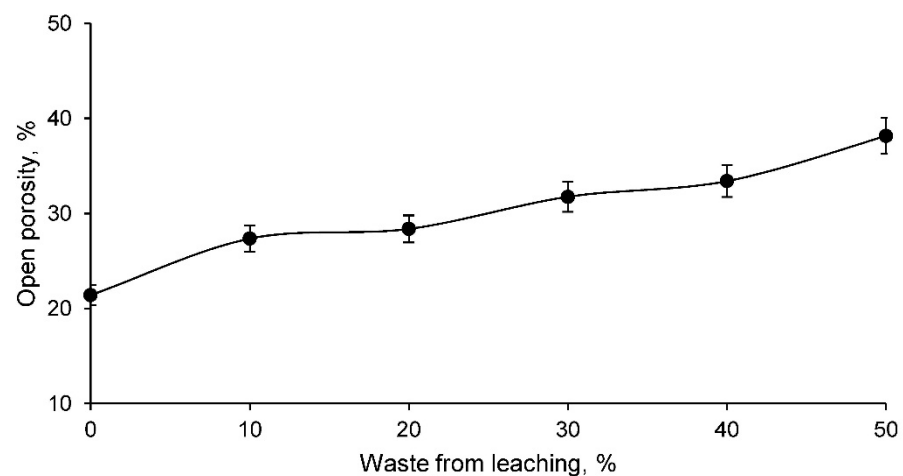


Figure 8. Open porosity of different clay-conformed ceramics families and leaching residue.

The open porosity of the clay-conformed ceramics with leach residue increases as the percentage of leaching residue increases. This was to be expected based on the test results detailed above and obviously conditions the strength of the material. However, higher porosity can improve certain properties of traditional ceramics such as thermal or acoustic insulation. Therefore, there is a wide variety of physical test results depending on the percentage of leaching residue in the ceramic, allowing to obtain ceramic materials for different applications.

Finally, the last physical property that characterizes the family of clay-conformed ceramics with leaching residue, bulk density, was calculated. The results of this test are shown in Figure 9.

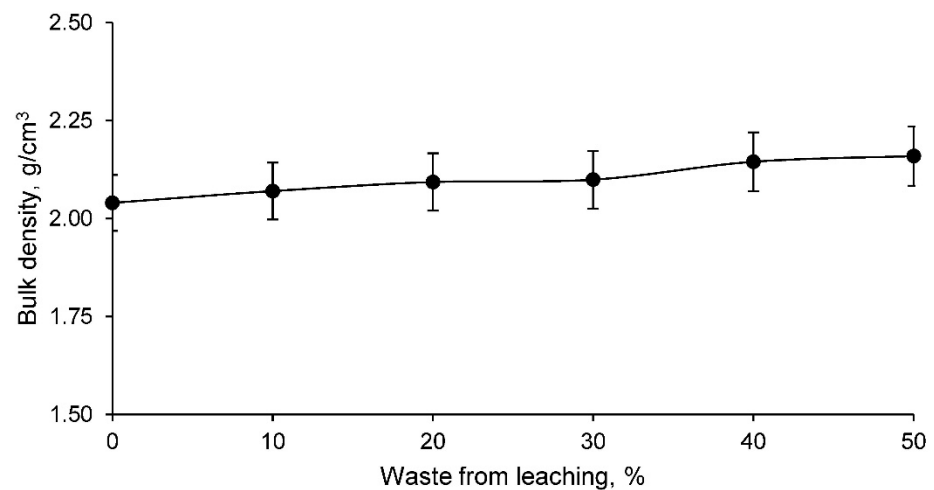


Figure 9. Bulk density of different families of clay-conformed ceramics and leaching residue.

The results shown in Figure 9 on bulk density show that the families of ceramics conformed with a higher percentage of leaching residue have a higher bulk density. This fact, far from being contradictory to previous tests in which a ceramic with higher porosity was observed, reflects the higher density of the leaching residue, which is to be expected if one takes into account the X-ray fluorescence test of this waste in which heavy metals appear in high proportion. Consequently, the ceramic conformed with a higher leaching residue, even presenting a higher porosity, has a higher apparent density due to the chemical composition of the waste.

Finally, to obtain the mechanical strength of the ceramics intended for construction bricks, Figure 10 shows the compressive strength of the various families of clay-conformed ceramics and the leaching residue.

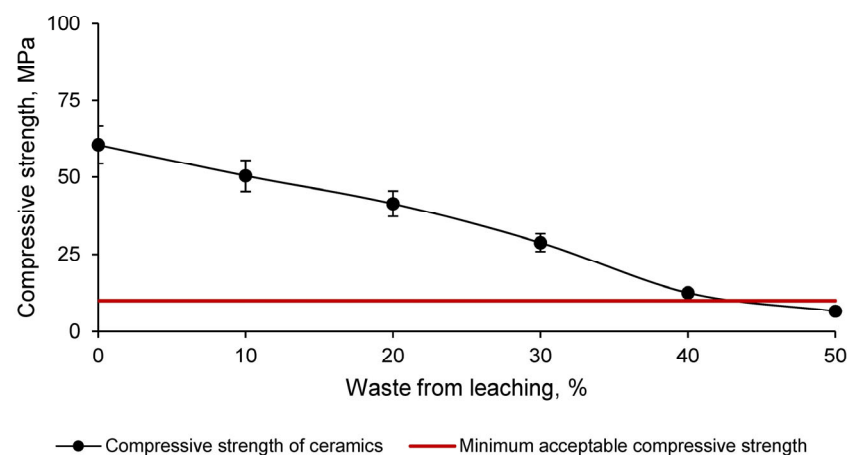


Figure 10. Compressive strength of different families of clay-conformed ceramics and leaching residue.

The compressive strength of ceramic materials intended for bricks is limited to 10 MPa according to European standards. Therefore, the family of ceramics conformed with 50% leaching residue and 50% clay is unusable. The other families of ceramics present compressive strengths higher than those established by the standards, taking into account that this strength decreases the higher the percentage of leaching residue in the ceramic. Consequently, the families conformed with clay and percentages of leaching residue of 10%, 20%, 30%, and 40% present physical and mechanical properties, according to the tests carried out, suitable for use in ceramic materials intended for the manufacture of bricks for construction.

4. Conclusions

The results of the tests mentioned in the methodology of this research allow us to obtain a series of partial conclusions that derive in the confirmation of the final objective. The final objective of this article is to extract by leaching in acid media, atmospheric pressure, and ambient temperature the zinc existing in the electric arc furnace dusts, as well as to reuse the leaching residue from the process as a raw material for ceramics. Consequently, the partial conclusions obtained are as follows:

- Electric arc furnace dusts contain a significant percentage of zinc, around 18%. This zinc seems to exist in the form of oxides, due to the formation process of this waste. There are also other elements such as iron (in high proportion), calcium, silicon, chlorine, sodium, magnesium, potassium, and manganese;
- The 0.5 and 1 molar sulfuric acid solutions leach the total percentage of zinc existing in the sample as determined by X-ray fluorescence analysis (188.3 mg/g). This leaching process was carried out with a solid/liquid ratio of 1:20, constant agitation, ambient temperature, and atmospheric pressure;
- The 1 molar solution of sulfuric acid leaches the zinc from the electric arc furnace dusts in its entirety in 36 h, according to the detailed procedure. Therefore, this solution was selected as optimal and a leaching time of 36 h was set;
- The waste produced in the leaching process with the selected dilution and time was chemically characterized, presenting a higher percentage of sulfur and hydrogen than the electric arc furnace dust. At the same time, the leaching residue contains other chemical elements such as iron (in high proportion), calcium, silicon, lead, aluminum, magnesium, and manganese. In addition, the percentage of zinc in the leaching residue was very low, corroborating the effectiveness of the leaching process;
- Ceramics conformed with clay and leaching residue showed a more open structure the higher the percentage of waste. Consequently, ceramics with leaching residue show lower linear shrinkage, higher capillary water absorption, higher cold water absorption, and higher porosity compared to that of a traditional ceramic consisting only of clay. However, the bulk density of ceramics conformed with the leaching residue increases as the percentage of waste increases, mainly due to the existence of heavy metals;
- The strength of ceramics conformed with clay and leaching residue from electric arc furnace dusts is lower the higher the percentage of waste, with unacceptable strength values for samples conformed with 50% clay and 50% leaching residue. Consequently, and according to the physical and mechanical tests carried out, the families of ceramics conformed with the leaching residue that are suitable for use are those incorporating 10%, 20%, 30%, and 40% of waste.

Based on the partial conclusions obtained, it is possible to leach the zinc existing in the electric arc furnace dusts in its entirety with sulfuric acid solutions, constant agitation, ambient temperature, and atmospheric pressure, mainly with the 1 molar solution of sulfuric acid and 36 h of process. Furthermore, with the waste from the leaching process, it is possible to manufacture ceramic materials for use as bricks with percentages of up to 40% of the waste, complying with European regulations in this respect for the tests carried out. This research is therefore an example of the potential that waste still has for the valorization of economically viable elements and their reuse as raw materials for new materials. Consequently, a new environmental hydrometallurgy is developed in which there is no waste and in which environmental pollution caused by the deposition of hazardous waste in landfills is avoided along with extracting new raw materials for the manufacture of ceramics.

Author Contributions: Conceptualization, F.A.C.-I., E.R.M.-L., J.M.T.-S. and J.S.-M.; methodology, F.A.C.-I., E.R.M.-L., J.M.T.-S. and J.S.-M.; software, J.M.T.-S. and J.S.-M.; validation, F.A.C.-I. and E.R.M.-L.; formal analysis, F.A.C.-I. and E.R.M.-L.; investigation, J.M.T.-S. and J.S.-M.; resources, F.A.C.-I.; data curation, E.R.M.-L.; writing—original draft preparation, J.S.-M.; writing—review and editing, J.M.T.-S.; visualization, J.M.T.-S.; supervision, F.A.C.-I.; project administration, J.S.-M.; funding acquisition, F.A.C.-I. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: In Technical and human support provided by CICT of Universidad de Jaén (UJA, MINECO, Junta de Andalucía, FEDER) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Graedel, T.E.; Harper, E.M.; Nassar, N.T.; Reck, B.K. On the materials basis of modern society. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 6295–6300. [[CrossRef](#)]
- Hagelüken, C.; Lee-Shin, J.U.; Carpentier, A.; Heron, C. The EU Circular Economy and Its Relevance to Metal Recycling. *Recycling* **2016**, *1*, 242–253. [[CrossRef](#)]
- Broadbent, C. Steel's recyclability: Demonstrating the benefits of recycling steel to achieve a circular economy. *Int. J. Life Cycle Assess.* **2016**, *21*, 1658–1665. [[CrossRef](#)]
- Madias, J. Electric Furnace Steelmaking. *Treatise Process Metall.* **2014**, *3*, 271–300.
- Naito, M.; Takeda, K.; Matsui, Y. Ironmaking Technology for the Last 100 Years: Deployment to Advanced Technologies from Introduction of Technological Know-how, and Evolution to Next-generation Process. *ISIJ Int.* **2015**, *55*, 7–35. [[CrossRef](#)]
- Jaimes, W.; Maroufi, S. Sustainability in steelmaking. *Curr. Opin. Green Sustain. Chem.* **2020**, *24*, 42–47. [[CrossRef](#)]
- Das, B.; Prakash, S.; Reddy, P.S.R.; Misra, V.N. An overview of utilization of slag and sludge from steel industries. *Resour. Conserv. Recycl.* **2007**, *50*, 40–57. [[CrossRef](#)]
- De Buzin, P.J.W.K.; Heck, N.C.; Vilela, A.C.F. EAF dust: An overview on the influences of physical, chemical and mineral features in its recycling and waste incorporation routes. *J. Mater. Res. Technol.* **2017**, *6*, 194–202. [[CrossRef](#)]
- Guézennec, A.G.; Huber, J.C.; Patisson, F.; Sessiecq, P.; Birat, J.P.; Ablitzer, D. Dust formation in Electric Arc Furnace: Birth of the particles. *Powder Technol.* **2005**, *157*, 2–11. [[CrossRef](#)]
- Gupta, S.; French, D.; Sakurovs, R.; Grigore, M.; Sun, H.; Cham, T.; Hilding, T.; Hallin, M.; Lindblom, B.; Sahajwalla, V. Minerals and iron-making reactions in blast furnaces. *Prog. Energy Combust. Sci.* **2008**, *34*, 155–197. [[CrossRef](#)]
- Agency, E.P. *European Waste Catalogue and Hazardous Waste List*; Environmental Protection Agency Ireland: Wexford, Ireland, 2002; ISBN 1840950838.
- Xanthopoulos, P.; Agatzini-Leonardou, S.; Oustadakis, P.; Tsakiridis, P.E. Zinc recovery from purified electric arc furnace dust leach liquors by chemical precipitation. *J. Environ. Chem. Eng.* **2017**, *5*, 3550–3559. [[CrossRef](#)]
- Martins, F.M.; Neto, J.M.; da Cunha, C.J. Mineral phases of weathered and recent electric arc furnace dust. *J. Hazard. Mater.* **2008**, *154*, 417–425. [[CrossRef](#)] [[PubMed](#)]
- Oustadakis, P.; Tsakiridis, P.E.; Katsiapi, A.; Agatzini-Leonardou, S. Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part I: Characterization and leaching by diluted sulphuric acid. *J. Hazard. Mater.* **2010**, *179*, 1–7. [[CrossRef](#)]
- Guo, X.; Zhong, J.; Song, Y.; Tian, Q. Substance flow analysis of zinc in China. *Resour. Conserv. Recycl.* **2010**, *54*, 171–177. [[CrossRef](#)]
- Yu, G.; Peng, N.; Zhou, L.; Liang, Y.J.; Zhou, X.Y.; Peng, B.; Chai, L.Y.; Yang, Z.H. Selective reduction process of zinc ferrite and its application in treatment of zinc leaching residues. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 2744–2752. [[CrossRef](#)]
- Su, Y.M.; Huang, W.C.; Liu, Y.C.; Chang, C.K.; Kuo, Y.L. Utilization of electric arc furnace dust as regenerable sorbents for the removal of hydrogen sulfide. *Ceram. Int.* **2017**, *43*, S694–S699. [[CrossRef](#)]
- Lin, X.; Peng, Z.; Yan, J.; Li, Z.; Hwang, J.Y.; Zhang, Y.; Li, G.; Jiang, T. Pyrometallurgical recycling of electric arc furnace dust. *J. Clean. Prod.* **2017**, *149*, 1079–1100. [[CrossRef](#)]
- Wang, J.; Zhang, Y.; Cui, K.; Fu, T.; Gao, J.; Hussain, S.; AlGarni, T.S. Pyrometallurgical recovery of zinc and valuable metals from electric arc furnace dust—A review. *J. Clean. Prod.* **2021**, *298*, 126788. [[CrossRef](#)]
- Youcai, Z.; Stanforth, R. Extraction of zinc from zinc ferrites by fusion with caustic soda. *Miner. Eng.* **2000**, *13*, 1417–1421. [[CrossRef](#)]
- Langová, Š.; Leško, J.; Matýsek, D. Selective leaching of zinc from zinc ferrite with hydrochloric acid. *Hydrometallurgy* **2009**, *95*, 179–182. [[CrossRef](#)]

22. Havlík, T.; Souza, B.V.E.; Bernardes, A.M.; Schneider, I.A.H.; Mišková, A. Hydrometallurgical processing of carbon steel EAF dust. *J. Hazard. Mater.* **2006**, *135*, 311–318. [[CrossRef](#)] [[PubMed](#)]
23. Zhang, L.; Liu, B.; Du, J.; Liu, C.; Wang, S. CO₂ emission linkage analysis in global construction sectors: Alarming trends from 1995 to 2009 and possible repercussions. *J. Clean. Prod.* **2019**, *221*, 863–877. [[CrossRef](#)]
24. Almeida, M.I.; Dias, A.C.; Demertzi, M.; Arroja, L. Contribution to the development of product category rules for ceramic bricks. *J. Clean. Prod.* **2015**, *92*, 206–215. [[CrossRef](#)]
25. Suárez-Macías, J.; Terrones-Saeta, J.M.; Iglesias-Godino, F.J.; Corpas-Iglesias, F.A. Retention of Contaminants Elements from Tailings from Lead Mine Washing Plants in Ceramics for Bricks. *Minerals* **2020**, *10*, 576. [[CrossRef](#)]
26. Terrones-Saeta, J.M.; Suárez-Macías, J.; Iglesias-Godino, F.J.; Corpas-Iglesias, F.A. Study of the incorporation of biomass bottom ashes in ceramic materials for the manufacture of bricks and evaluation of their leachates. *Materials* **2020**, *13*, 2099. [[CrossRef](#)] [[PubMed](#)]