

Article

Study of Copper Leaching from Mining Waste in Acidic Media, at Ambient Temperature and Atmospheric Pressure

Juan María Terrones-Saeta *¹, Jorge Suárez-Macías¹, Francisco Javier Linares del Río and Francisco Antonio Corpas-Iglesias¹

Department of Chemical, Environmental, and Materials Engineering, Higher Polytechnic School of Linares, University of Jaen, Scientific and Technological Campus of Linares, 23700 Linares, Spain; jsuarez@ujaen.es (J.S.-M.); fjlr0015@red.ujaen.es (F.J.L.d.R.); facorpas@ujaen.es (F.A.C.-I.)

* Correspondence: terrones@ujaen.es; Tel.: +34-675-20-939

Received: 24 August 2020; Accepted: 29 September 2020; Published: 1 October 2020



Abstract: Mining activity produces a series of wastes that must be treated to avoid environmental pollution. In addition, some of these mining wastes still contain metallic elements that are interesting for their extraction with new less expensive techniques and that can work with low mineral grades, such as hydrometallurgy. This study evaluates the suitability of Copper recovery in mining wastes, coming from waste dump, with a high percentage of metal oxides and granite. This recovery is carried out through leaching in 0.05, 0.10, 0.15 and 0.20 molar Sulphuric Acid solutions, at ambient temperature and atmospheric pressure. The exposure of the waste to the solution was made for 96 h, taking measurements of the leaching and evaluating the increase in Copper concentration every 24 h. The results reflected a good Copper recovery rate with concentrations up to 1.9 g/L. The best results were obtained for the 0.20 molar Sulphuric Acid solutions, producing a stability in the Copper concentration after 72 h. Other elements in smaller proportion as the Zinc were also recovered. Therefore, a process of recovery of Copper was obtained with a robust, versatile and economic technique in mining residues that currently represent an environmental pollution.

Keywords: hydrometallurgy; leachate; ICP-MS; polymetallic sulphides; granite; copper; mining waste; waste rock; recovery rate; sustainability

1. Introduction

Copper is one of the most demanded materials nowadays. This fact is mainly due to its use in several areas, such as in information, energy, electronics, construction, the military, shipping, railway, etc. [1]. The use in different areas is due to its properties and versatility, presenting very good electrical conductivity, thermal conductivity, malleability, resistance to chemical agents and, in addition, being easily combined with other elements to obtain alloys with very particular characteristics, widely used in construction.

Therefore, Copper is a strategic material for different countries, as there is a significant imbalance between supply and demand. An example is China, which for years is the largest consumer of Copper in the world, [2], obtaining this material mainly from Copper Sulphide minerals. These Copper Sulphide minerals are treated in 98% with pyrometallurgical techniques [3]. However, the protection of natural resources, low mineral grades and an excessive increase in demand means that these techniques are no longer as profitable as in the past. On the other hand, Copper is one of the 100% recyclable materials, so countries such as China are opting for the treatment of industrial waste [4], scrap metal and electronic waste to obtain Copper [5]. However, these recycling processes involve a significant

consumption of energy and natural resources, and therefore cause a considerable environmental impact, as well as that caused by the usual pyrometallurgical techniques for Copper processing.

Worldwide, 80% of copper is obtained by pyrometallurgical processes and only 20% by hydrometallurgical techniques, derived from processing mainly Copper Sulphide mineral [6]. However, due to the existence of decreased mineral laws, more restrictive environmental regulations and significant pollution due to the processes, makes pyrometallurgical techniques unprofitable. It is therefore necessary to develop hydrometallurgical processes that obtain Copper with lower energy consumption and in materials with much lower grades, such as industrial by-products, waste, mining waste, etc. In other words, to obtain Copper mainly from different raw materials impossible to concentrate by pyrometallurgical techniques [7], either because Copper is found in such low proportions that it is not economically viable or because it contains chemical elements that restrict its concentration, such as Arsenic, or because they are polymetallic minerals impossible to treat by traditional methods [8].

Therefore, it is the hydrometallurgical techniques that must be developed and implemented to provide the solutions to the problem of Copper demand. These techniques are economically viable and, as associated with their slow and low recovery, there are much lower processing costs than in pyrometallurgical techniques. However, they have not yet been commercially applied for landfills for ore or industrial waste [9].

There are new hydrometallurgical techniques for recovering Copper from Copper Sulphide minerals [10,11]—mainly chalcopyrite, with acidic solutions and at atmospheric pressure [12]. These new techniques have some essential advantages, on the one hand, their economy, as they are much slower processes and require less technology, so the cost of the equipment is reduced considerably; on the other hand, their versatility makes them applicable to almost any type of mineral independent of the impurities that they contain already, such as Zinc, Lead, Arsenic, Antimony, Mercury, etc. [13]. Another advantage is its simplicity, a series of parameters must be controlled periodically for its success but its implementation is simple and easy to maintain [14]—in short, its robustness as a technique, and being able to process diverse minerals with different chemical elements and coming from diverse formations. It is therefore a technique that is currently being evaluated in depth in the laboratory but that must be implemented commercially [15].

At the same time, it must be recognized that it has a series of disadvantages with respect to pyrometallurgical processes that need to be mentioned and evaluated [16]. In terms of production, and based on different case studies, it is difficult to fully recover Copper and the precious mineral; in terms of product quality, the leachate may not always contain a high proportion of Copper depending mainly on the solution, time and mineral used; variation in recovery rates is common, depending obviously on the minerals processed and their activity. Regarding the production of waste, it is therefore necessary to parallel research projects to this technique that are able to process the waste in order to obtain a process as sustainable as possible. Finally, there is the scarcity of equipment adapted to this technique compared to pyrometallurgical techniques, mainly due to its poor implementation. However, the advantages mentioned above represent a very wide field of research that may lead to an important development of hydrometallurgical techniques in the future, with its consequent implementation. In addition, as mentioned above, the low quality of the leached product, in some cases, is solved by the low cost of the initial material, the low cost of the process and the existing demand for Copper.

The recovery rate for hydrometallurgical techniques depends on several factors. These factors must be controlled in the process to optimize production and evaluate viability, even more so in the recovery of copper from landfills, which is the fundamental idea on which this project is based. The factors on which the Copper recovery rate depends are the following:

- The Copper minerals present. Obtaining Copper from mining waste by hydrometallurgical techniques is obviously influenced by the percentage of Copper minerals present. Usually they will be in combination with other types of minerals without value in greater or lesser proportions. At the same time, not all Copper minerals produce the same recovery rates, so it is interesting

for its classification and quantification. Impurities will also influence the recovery of Copper, although never to the same extent as in pyrometallurgical processes.

- The mineral associations in the existing rocks in the landfills and the easy release of the Copper minerals. There must be an initial study of the landfill to evaluate this factor directly related to that mentioned above.
- The particle size to be processed [17]. The absence of a concentrate in the mining waste and the combination with other non-valuable minerals means that leaching does not occur at its maximum recovery rate if these Copper minerals are not in contact with the acidic solution. Therefore, a crushing of the landfill materials will influence a higher probability of contact of the Copper ores with the acidic solution and, consequently, will result in a higher recovery rate. The crushing process is therefore essential if the aim is to obtain the highest recovery rate in the shortest time [18]. At the same time, it must be taken that milling very fine crushing would damage the industrial process, due to problems in the recirculation of the leachate and the creation of contaminating sludges. These sludges produced should be evaluated and reused in other industrial processes to avoid their deposition in landfills and the associated environmental pollution. In other words, it is important to evaluate the appropriate particle size to obtain an adequate recovery rate, a lower amount of contaminating waste and a more energetically optimized leaching process [19,20].

On the basis of the above, it is necessary to develop new hydrometallurgical techniques, at atmospheric pressure and in an acidic media [21], with different types of raw materials for various reasons. These reasons are the satisfaction of the demand, the implementation of new strategic industries, the search for particular solutions, the reduction in the environmental impact associated with the traditional processes and the optimization of the natural resources.

In addition, the use of waste as a material for the extraction of elements, such as those as important today as Copper, makes the development of a sustainable industry possible [22]. This industry reduce pollution from the deposition of these wastes, reduces the extraction of new virgin materials and provides economically viable solutions [23]. In this study, therefore, a process is developed within the circular economy.

With the detailed purpose, this work studies the recovery of Copper by hydrometallurgical techniques through the leaching in Sulphuric Acid solutions of materials coming from Lead mining landfills. To this end, the mine that is producing these dumps is initially characterized, the mineralogy of the existing landfills is evaluated, and representative samples are taken. These samples were chemically analyzed for the presence of Copper, as well as other chemical elements that could damage the recovery rate. Later, the samples were crushed to obtain an adequate particle size and it was subject to different solutions of low molar Sulphuric Acid for 4 days. Leachate samples were taken from all the solutions every 24 h and the recovery rate of Copper was evaluated as a function of time and the molar of the solution. In turn, were analyzed the presence in the leachate of the other secondary chemical elements or harmful chemical elements.

The results showed a concentration of Copper in the 0.20 molar solution of Sulphuric Acid maximum which was stable at 72 h. The recovery rate corresponding to this concentration value is approximately 80%. At the same time, interesting concentrations of other elements, such as Zinc, were obtained, with almost total recovery rates. The elements harmful to the process were in low proportion, among them Arsenic.

2. Materials and Methods

This section describes the material used for the extraction of Copper from Lead and Silver mine waste dumps, as well as the methodology followed to evaluate the suitability of Copper recovery by hydrometallurgy, based on leaching in acidic media of the minerals, at atmospheric pressure and ambient temperature.

2.1. Materials

The material evaluated for the extraction of Copper by leaching in acidic solutions comes directly from waste dumps in the mining district of Linares, Jaén. The mining activity of Linares was mainly focused on the extraction of Lead and in a smaller proportion the Silver from the galena argentiferous mineral present in the area. This mining activity was maintained for hundreds of years when Lead was an essential material for the population and there was a high demand for it. In the last few decades of the 20th century, the brutal fall in Lead prices, as well as the need for research into new exploitable seams, led to the total closure of mining activity. Therefore, there are different mining wastes from this intense mining activity that can be found throughout the mentioned territory, waste from washing plants, flotation or the waste landfill under study.

These mining wastes cause significant environmental pollution, as previous mining legislation did not provide for adequate environmental measures to be taken to avoid this. Therefore, it is usual that there is contamination of underground water and surface water by the Lead present in the waste, as well as other chemical elements, such as Arsenic, Sulfur, Zinc, etc. In turn, waste with smaller particle size causes a direct effect on vegetation. The impact of these enormous waste deposits notably affects the image of the territory, even though this has already been accepted by the majority of the population.

In these wastes, as mentioned, there is a high proportion of Lead. There are also contaminating elements that should be retained and, at the same time, minerals rich in chemical elements that can be profitable and which are currently in great demand—in this particular case, Copper.

In particular, the residue evaluated for the extraction of Copper belongs to the waste dump of the Lead extraction from the seam called “EL COBRE”. This reef of about 4500 m in length crosses the towns of Guarroman, Linares and Bailen. The seam is located in the direction of the most generalized fractures of the rock that forms it, this being mainly granite and, in the lesser half, very metamorphosed shale. This seam, from which the Lead mineral was extracted in the past, has an arrangement close to vertical with runs of up to 3000 m. The thickness of the same Lead usually oscillates between centimeters and several meters, it being usual that this was between one or two meters. The main minerals existing in the seam are the argentiferous galena, blende, Iron Sulphides (mainly pyrite) and Copper Sulphides, mainly chalcopyrite. This last mineral is the one of interest in the study. Figure 1 shows the image of the waste dump, as well as the particles that form it; their diversity and different sizes.

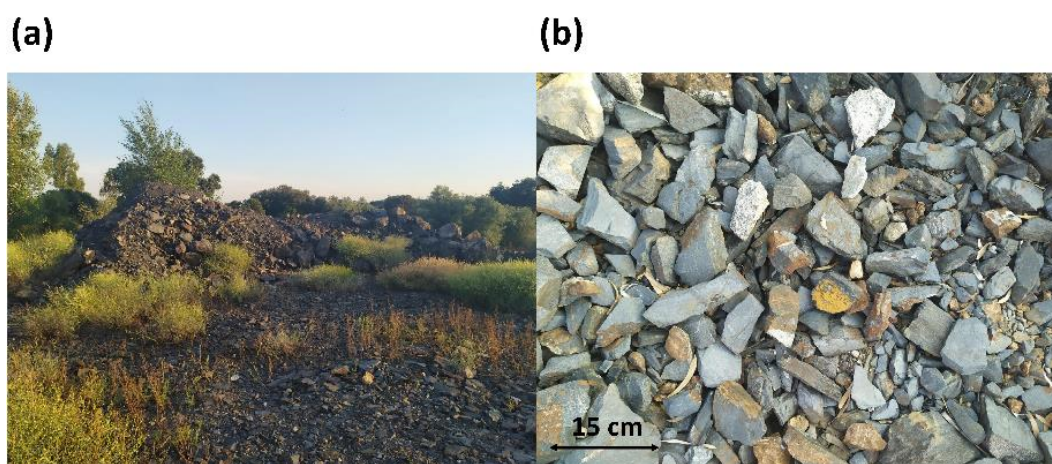


Figure 1. Image of the “EL COBRE” seam waste dump. (a) General image of the waste dump and (b) detailed image of the different particles that make it up.

The seam of “EL COBRE”, from which the study of its waste dumps is based and which has the name of the element to be extracted, has never been used for the extraction of Copper, only Lead and Silver were extracted in a much smaller proportion. Therefore, in its waste dumps it is easy to find

the Copper Sulphides that have not been processed. These Copper Sulphides have been transformed in most cases into Copper Oxides, due to the treatments carried out and the exposure over decades to the atmospheric conditions. The grades obtained by the mining company during the extraction and processing of this vein are variable, given its depth and thickness, being between 4.5% and 6% for Lead. In turn, the Silver contents were modest, being these between 240 and 360 grams of metal per ton of Lead recovered.

The exploitation of the “EL COBRE” seam at present, as has been commented on, is totally paralyzed, with almost all the reserves having been extracted. Underground mining was used and the mentioned minerals were processed to extract Lead later by gravimetric methods. The waste rock materials from lead extraction were deposited in large waste dumps, which are distributed along the course of the seams. In these waste dumps are found the Copper Oxides from the seam combined with the other minerals.

The waste dumps have a fairly random particle size, with particles of 10 to 15 cm predominating. The existing mineralogy is easily observable in these particles, this being mainly granite (rock that forms the seam), Copper Oxides, Iron and Lead Oxides. Different representative samples were taken from these waste dumps so that they could later reflect, in the laboratory, the composition and the real process that could be carried out in industry.

The samples taken from the “EL COBRE” seam waste dumps were first dried in an oven to remove any moisture they might contain and thus not influence the subsequent process with uncontrolled variables. However, the existence of humidity in the industry would not be detrimental to the hydrometallurgical process, but should be taken into account so that the acidic solutions were suitable and marked by research.

Later, the samples will be prepared differently for the leaching process or for the initial characterization, detailing such processes in the methodology.

2.2. Methodology

Once the origin of the waste to be analyzed for the extraction of Copper by hydrometallurgical methods was determined, the tests carried out to assess the suitability of this study were detailed. The methodology was a series of logical, structured and ordered tests capable of objectively evaluating the final conclusion of the study, as well as determining those key points on which greater attention must be paid in order to obtain acceptable results.

Once the mineralogy of the waste dump under study had been evaluated in situ, and the main minerals detailed in the previous section had been identified, the procedure was that representative samples were taken. The samples from the waste dump belonging to the mining waste mentioned above were dried for 24 h at a temperature of 105 ± 2 °C to eliminate the humidity.

Subsequently, the chemical characterization of the waste was necessary to study its chemical composition, as well as the Copper content present in the samples. The first test carried out was the elemental analysis for the detection of the chemical elements Carbon, Nitrogen, Hydrogen and Sulfur. Secondly, the loss on ignition test was performed, and finally, the X-ray fluorescence test, for the determination of the chemical elements with the highest atomic weight, including Copper.

After evaluating the chemical composition and determining the percentage of Copper present, leaching was carried out in acid solution. For this purpose, recirculation equipment was prepared in which the sample was introduced, and the watering of the same sample was executed continuously. The solution of Sulphuric Acid was achieved with four low molarities, in order to avoid high molarities that could lead to greater environmental pollution. In the different recirculation equipment, with different Sulphuric Acid solutions, measurements were taken every 24 h up to a total of 96 h. All leachate samples of the waste, in the four solutions and for the different times, were analyzed in the equipment, called the ICP-MS Instrument. In this way, the percentage of Copper present in all the samples was studied quantitatively, as well as that of other chemical elements that could be interesting.

With the results obtained, the ideal time of leaching and the adequate solution of Sulphuric Acid was determined, determining the viability of the study.

All the above-mentioned tests are described in two large blocks, analysis of the chemical composition of the waste and the leaching process and measurement of the concentration. These blocks are described in more detail below.

2.2.1. Analysis of the Chemical Composition of the Waste

The analysis of the chemical composition of the waste to be processed by leaching techniques in acidic media is essential. The aim is to determine the percentage of Copper present in the sample tested, as well as the existence of other chemical elements that may be harmful to this leaching process. The chemical composition of the dump waste will confirm that the chemical elements present coincide with the minerals identified.

Based on the above, the first of the tests is the elemental analysis test, performed with TruSpec Micro equipment (LECO, St. Joseph, MI, USA) from the LECO brand. This test consists of the combustion of the sample at a temperature of 1000 ± 10 °C and the analysis of the gases produced, analyzing the chemical elements of Carbon, Nitrogen, Hydrogen and Sulfur. The residue sample, as it has a mainly inorganic composition, will present relatively low percentages of these elements. However, the percentage of Carbon will reflect the percentage of organic matter and carbonates. On the other hand, the Sulfur present will show the percentage of the sulphurous minerals. However, not all the percentage of Sulphur determined by elemental analysis will be the existing one, since combustion takes place up to 1000 ± 10 °C, existing at a higher percentage determined by X-ray fluorescence (Thermo Fisher Scientific, Waltham, MA, USA).

In turn, the loss on ignition test reflects the change in weight after the sample has been subjected to the temperature of 1000 ± 10 °C. This loss of weight, at the above mentioned temperature, corresponds mainly to the loss of weight by the percentage of organic matter, the loss of weight by the percentage of carbonates, the transformation of some chemical compounds as well as the oxidation of other chemical elements. It is therefore difficult to assess which aspect they correspond to; however, this test provides sufficient information in correlation with the other tests.

Finally, the X-ray fluorescence test on the waste sample from the "EL COBRE" seam waste dump will provide the composition of the remaining chemical elements not analyzed in the elemental analysis. This test is essential to determine the percentage of Copper in the sample, as well as to corroborate the chemical composition predicted by the mineralogical study determined in the previous section. That is, the chemical composition must correspond to the chemical elements of the minerals present in the waste sample. In turn, it will determine the percentage of contaminating or conflicting elements for the leaching process that could damage the complete and rapid leaching of the Copper. Among these chemical elements are Arsenic, Zinc, Lead, Iron, etc.

2.2.2. Leaching Process and Concentration Measurement

After analyzing the chemical composition of the waste dump from the "EL COBRE" seam, we proceeded to study the leaching of Copper with different solutions of Sulphuric Acid, at different times of leaching and with atmospheric pressure.

First the samples were crushed until a particle size between 6 mm and 10 mm was obtained. The crushing of the sample and obtaining this size is based on several factors. Firstly, this process is carried out in such a way that the Copper ore is in contact with the solution on the greatest possible surface, since, as has been mentioned, this ore appears associated with other minerals and even with the conforming rock that is granite. If the mineral is encapsulated, the leaching process in an acidic media is slower and not as effective since the solution must penetrate to leach the existing Copper. Therefore, initial particle sizes around 10 cm and 15 cm are discarded. On the other hand, a very fine particle size would favor the leaching process but would create sludges, this fact being a detriment to the continuous recirculation of the solution and causing a higher energy expenditure. At the same

time, these sludges produced should be separated and finally treated, since it is a polluting waste that cannot be directly deposited in a landfill. In short, the particle size selected is that which will provide an adequate recovery rate and, in turn, very low percentages of waste sludges.

The mining waste samples with particle size between 6 mm and 10 mm were divided into subsamples of similar composition to perform the most objective leaching analysis possible. The UNE-EN 932-2 standard was used for the subdivision. This process is very important, since obtaining similar samples will significantly influence the quality of the results.

Once the sample had been crushed and the desired particle size had been obtained, the leaching test was carried out in an acidic media and with different solutions. The samples selected for leaching had a mass of 10 ± 0.1 g and were previously dried to remove humidity.

On the other hand, the Sulphuric Acid solutions were 0.05, 0.10, 0.15 and 0.20 molar. The use of these low molar solutions is motivated by different factors; firstly, the use of low molar Sulphuric Acid solutions will create a more easily treatable residue, respecting the sustainability of the process in a global way and avoiding unnecessary contaminating residues. On the other hand, higher molars could lead to excess sludge creation without providing a higher extraction rate. Finally, solutions with higher concentrations of Sulphuric Acid would create a greater leaching of other chemical elements that could damage and disturb the subsequent processes for the extraction of Copper, increasing the percentage of Iron, Magnesium, Arsenic, etc. in the leachate.

The leaching process was carried out in equipment specially prepared for this study. This very simple equipment consisted of an airtight container wherein the sample was poured. Below the sample there were two filters—one of 1 mm, to avoid release particles larger than that size during the leaching process, and another of 0.1 mm, to try to retain the sludge derived from the leaching process. At the same time, there was a lower intake from which the solution was taken and pumped to the top for the continuous irrigation of the waste sample. This process is kept constant during the 96 h of the test, without interruption and controlling the temperature at 25 ± 1 °C. The container was large enough to hold the samples and 200 ± 1 mL of each of the solutions. The image of the equipment can be seen in Figure 2.

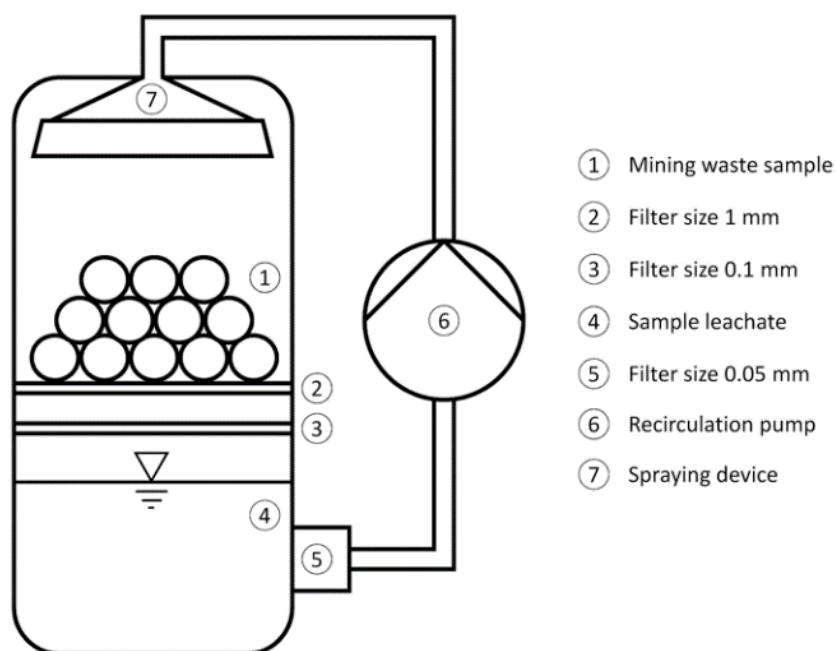


Figure 2. Equipment for leaching mining waste in an acidic media, ambient temperature and atmospheric pressure. Own elaboration.

Once the four solutions were made, the four processes were started with the four similar samples of waste from the “EL COBRE” seam. Every 24 h, we proceeded to take samples of leaching of the four solutions of Sulphuric Acid, as well as the continuous corroboration of the temperature. In this test, a total of 4 repetitions was carried out for each solution.

The samples obtained were analyzed in the ICP-MS of the commercial brand Agilent model 7900 (Agilent Technologies, Santa Clara, CA, USA). For the quantification of the percentage of Copper and the other chemical elements with higher precision, patterns of Copper and the other elements under study were used.

3. Results and Discussions

This section describes the results of all the tests mentioned in the methodology. From each test, partial conclusions were drawn that to help reach a final conclusion. The final conclusion is the evaluation of the suitability of leaching of mining waste from waste dumps by acidic media, at ambient temperature and atmospheric pressure, for the recovery of Copper. The above-mentioned tests are presented in the two large blocks mentioned.

3.1. Analysis of the Chemical Composition of the Waste

The chemical composition of the waste of the dump waste under study must be characterized for various reasons. On the one hand, for the knowledge of the percentage of Copper existing in the sample; on the other hand, for the evaluation of the chemical elements that can damage the leaching process; finally, the study of other interesting elements to leach in a smaller proportion.

For this purpose, the study was performed with the sample prepared according to the methodology—the elemental analysis test. The elemental analysis test is reflected in Table 1.

Table 1. Elemental analysis Carbon, Hydrogen, Nitrogen and Sulfur for mining waste.

Samples	Nitrogen, %	Carbon, %	Hydrogen, %	Sulfur, %
Mining waste	0.001 ± 0.002	3.735 ± 0.051	0.393 ± 0.014	0.647 ± 0.024

The elemental analysis of the mining waste sample shows a very low percentage of Carbon. This low percentage of Carbon confirms the low proportion of organic matter and carbonates. By this analysis, it is difficult to identify specifically what it is; however, the value is adequate and does not present problems. The low percentage of Hydrogen may be due to the transformation of hydrated compounds or to the unavoidable residual humidity from the test process. However, as with Carbon, this value is quite small. Finally, it can be seen that there is a percentage of Sulfur evaluated by means of this test in the gases analyses of the combustion of the sample at 1000 ± 10 °C. The existence of this low percentage of Sulphur reflects the transformation of primary minerals, Polymetallic Sulphides, into oxides. However, it should be noted that the percentage of Sulfur determined by elemental analysis is not the total of that existing in the sample. Subsequently, we evaluated the percentage of Sulfur remaining by the X-ray fluorescence method.

The loss of ignition test reflects the change in weight of the sample when it is subjected to a temperature of 1000 ± 10 °C. This variation in weight is due to different reasons. On the one hand, the loss of Carbon from organic matter and carbonates; on the other hand, the loss of the most volatile chemical elements, such as Hydrogen, Nitrogen and Sulfur. Finally, it is due to the transformation of some chemical compounds and the oxidation of the chemical elements. The loss of ignition of the mining waste sample under study is $19.28 \pm 0.36\%$. This loss of ignition, after observing the reduced percentages shown by the elemental analysis of the elements analyzed, is mainly due to the transformation of minerals and their oxidation. This process that was carried out was the one commonly used in hydrometallurgy for leaching the treatment of chalcopyrite in acidic media, also called roasting. The value of loss on ignition is usual and similar to those obtained in tests of this type for residues.

X-ray fluorescence determined the percentage of the chemical elements the highest atomic weight. For this purpose, the test was carried out on the calcined sample at a temperature of 1000 ± 10 °C. This procedure was carried out because the equipment was not capable of detecting chemical elements, such as Carbon, so if it was not carried out with the calcined sample, the X-ray fluorescence equipment would distribute the percentage of chemical elements detected without taking this into account, and therefore with an error. The results of the X-ray fluorescence test performed on the mining waste sample after the loss on ignition test are shown in Oxygen compounds, because they have been transformed. The results of the X-ray fluorescence test are shown in Table 2.

Table 2. X-ray fluorescence of the mining waste sample.

Compound	wt, %	Est. Error
CaO	31.40	0.23
SiO ₂	19.49	0.20
Fe ₂ O ₃	9.01	0.14
Al ₂ O ₃	6.10	0.12
CuO	5.85	0.12
MgO	2.73	0.08
K ₂ O	1.52	0.06
MnO	1.37	0.06
PbO	1.06	0.05
ZnO	0.989	0.049
S	0.440	0.022
TiO ₂	0.317	0.016
BaO	0.209	0.010
P ₂ O ₅	0.0704	0.0035
NiO	0.0354	0.0018
As ₂ O ₃	0.0353	0.0026
Co ₃ O ₄	0.0179	0.0013
SnO ₂	0.0159	0.0014
SrO	0.0149	0.0007
Cr ₂ O ₃	0.0140	0.0014
ZrO ₂	0.0117	0.0009
Y ₂ O ₃	0.0114	0.0008
Rb ₂ O	0.0111	0.0006
CdO	0.0088	0.0010
V ₂ O ₅	0.0042	0.0015
Ag ₂ O	0.0024	0.0009

The results in Table 2 reflect the chemical composition of the mining waste in oxide compounds; therefore, we proceeded to eliminate the Oxygen and recalculate the percentage of the chemical elements present in the mining waste sample, obviously taking into account the percentage of Oxygen. The elemental composition of the mining waste obtained by X-ray fluorescence is shown in Table 3.

Table 3 shows the percentage that the different chemical elements analyzed present in the sample, as well as the percentage of Oxygen due to the oxides present in the mining waste after oxidation in the calcination process. The sum of all the elements, plus the Oxygen and the loss of ignition reflects 100% of the sample; therefore, this method is the most reliable for the determination of the real percentage of each of the chemical elements that exist in the sample, independent of their combination in different chemical compounds.

Table 3. Elementary chemical composition obtained by X-ray fluorescence from the mining waste sample.

Element	wt, %	Est. Error
Ca	22.45	0.17
Si	9.11	0.09
Fe	6.30	0.10
Al	3.23	0.06
Cu	4.67	0.09
Mg	1.65	0.05
K	1.26	0.05
Mn	1.06	0.05
Pb	0.98	0.05
Zn	0.794	0.040
S	0.440	0.022
Ti	0.1900	0.0095
Ba	0.1870	0.0093
Px	0.0307	0.0015
Ni	0.0278	0.0014
As	0.0267	0.0020
Co	0.0132	0.0009
Sn	0.0125	0.0011
Sr	0.0126	0.0006
Cr	0.0096	0.0010
Zr	0.0087	0.0006
Y	0.0090	0.0006
Rb	0.0101	0.0005
Cd	0.0077	0.0009
V	0.0023	0.0008
Ag	0.0022	0.0009
Total Weight% Oxygen	28.23	0.33

In view of the results, it can be seen that the percentage of Copper, the main element of this study, is $4.67 \pm 0.09\%$. This Copper is the one that is intended to be extracted by leaching in acidic media at atmospheric pressure and ambient temperature. The percentage of Copper is contemplated as a viable percentage for its recovery; that is to say, it is not a reduced percentage, but it would be if presenting problems to be extracted by pyrometallurgical means. This fact is due to the diversity of existing minerals, the combination of them and the existence of some harmful elements for the pyrometallurgical process that will be detailed later. In short, the present percentage of Copper for the development of this new hydrometallurgical technique is correct and be expected from the material to which it corresponds.

Calcium represents a high percentage in the composition, corresponding to feldspars and granite mica, as does Aluminium. It should be remembered that granite is the main rock in which metallic sulphide deposits have been formed, so its presence in the waste dump is important. However, Calcium and Aluminum are not chemical elements that harm the hydrometallurgical leaching process, so they are not a problem. Similarly, silicon is present in a significant percentage as granite is a siliceous rock.

The Magnesium, Manganese and Potassium, as in the previous cases, come directly from the granite, and it is not unusual to find them in the percentages detailed in this rock.

Lead comes from the galena, a mineral mainly extracted in the mine workings of the seam. The percentage of Lead is reduced, as the waste belongs to the waste dumps of the waste rock materials of the mine, so the mining process drastically reduced the percentage of Lead in the waste. In a much smaller proportion, Silver appears, associated to Lead in the argentiferous galena mineral.

Zinc, belonging to the blende mineral and recognized in the process of mineralogical study, appears in low proportion in the composition. Therefore, it is not the main element of extraction by

leaching in acidic media, but it can be an extracted in lower recovery rate after obtaining Copper, also being an element quoted by the industry.

The other chemical elements are in very small proportion, making wet process tests necessary to quantify them under higher precision. It is common to find, in these types of mining formations, Arsenic Sulphides that would seriously damage the pyrometallurgical process; however, in hydrometallurgy, its influence is much smaller and the percentage it represents in the mining waste is very low. It should be noted that the low percentage of Sulphur reflects the transformation and oxidation of the Polymetallic Sulphides mentioned by the action of the atmospheric conditions.

In short, the percentage of Copper existing in the sample, and the inexistence of chemical elements that could damage the process in high percentages, make possible and viable the subsequent leaching section of the sample in acidic media at atmospheric pressure and ambient temperature, based on hydrometallurgical techniques.

3.2. Leaching Process and Concentration Measurement

The chemically characterized mining waste sample was then divided into several subsamples. These subsamples were subjected to the leaching process with the equipment detailed in Figure 2, with different solutions of Sulphuric Acid, 0.05, 0.10, 0.15 and 0.20 molar. The process was carried out at ambient temperature (25 ± 1 °C) and atmospheric pressure for 96 h, taking samples of the leachate every 24 h. It should be noted that, at the end of the leaching process, no sludge was found at the bottom of the vessel, confirming the suitability of the sample grading for this purpose.

Firstly, and as a main element of study, the concentrations of Copper in the leachate for the four Sulphuric Acid solutions and at different leaching times are detailed in Figure 3.

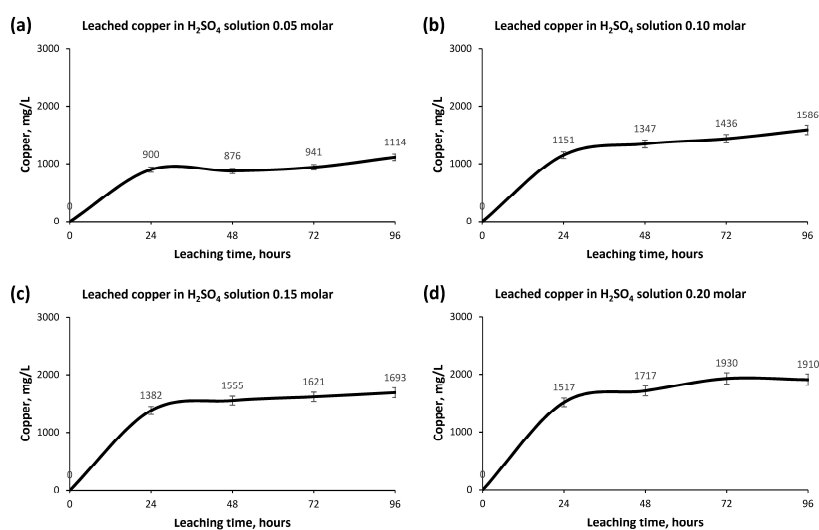


Figure 3. Analysis of Copper concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H_2SO_4 solution, (b) 0.10 molar H_2SO_4 solution, (c) 0.15 molar H_2SO_4 solution, (d) 0.20 molar H_2SO_4 solution.

As can be seen in Figure 3, the concentration of Copper in the leachate is higher for the 0.20 molar Sulphuric Acid solution, the concentration being progressively higher with the increasing molar of the solution. Sulphuric Acid solutions of 0.05 molar, 0.10 molar and 0.15 molar, reflect the fact that there is no stabilization in the leach after 96 h, with a reduced upward slope in all three solutions. Therefore, more time leaching is necessary to achieve the results of the 0.20 molar of Sulphuric Acid solution. On the other hand, in the solution of 0.20 molar of Sulphuric Acid, if there is a stabilization of the concentration after 72 h, it shows very similar values of Copper concentration after a longer times.

In turn, most of the Copper leaching occurs in the first 24 h of the process and for the four Sulphuric Acid solutions. The percentage increase in Copper concentration after the first 24 h is about 20%.

The results reflect a better behavior of the 0.20 molar Sulphuric Acid solution because it needs a shorter leaching time, as well as a stabilization of the concentrations at 72 h. Taking into account the mass of the sample tested, the volume of the solution and the percentage of Copper in the sample, it can be stated that, under the prescribed conditions and with the detailed equipment, there is an approximate recovery of 82% of the Copper in the sample with the 0.20 molar solution of Sulphuric Acid. It is therefore a good result of copper extraction given the material it comes from (mining waste), the leaching conditions (atmospheric pressure and ambient temperature), the low molar of Sulphuric Acid of the solution and the more economical extraction process.

Higher values of Copper recovery rates would require higher concentrations of Sulphuric Acid and the smaller particle sizes of the sample. This would negatively affect the principles of this study, since we would create a leachate with higher Sulphuric Acid and it would be more difficult to treat, as well as a higher percentage of sludge that would damage the leaching process and subsequently be very difficult to reuse due to its environmental pollution. In addition, it is important to note that a concentration of almost 2 g/L of Copper was obtained, this being an acceptable value for classical hydrometallurgical techniques with Copper Oxide minerals and viable for subsequent treatment of the extraction.

The results of the Copper concentrations of the four Sulphuric Acid solutions, at different times and in the mentioned leaching process, are reflected for comparison in Figure 4.

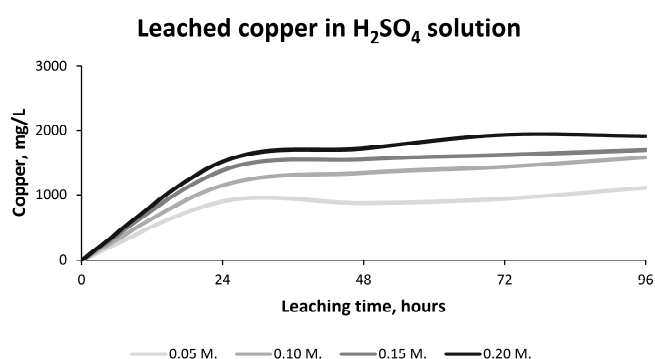


Figure 4. Comparison of the Copper concentrations in the four Sulphuric Acid solutions with different leaching times and leaching process at ambient temperature and atmospheric pressure.

Figure 4 shows the comparison of the Copper concentration in the three leachates, reflecting the existence of a great similarity between the 0.10, 0.15 and 0.20 molar Sulphuric Acid concentrations, taking into account the detail commented on before the non-stabilization of the Copper concentration in the time evaluated for the 0.10 and 0.15 molar Sulphuric Acid solutions. They are, therefore, the three acceptable solutions of Sulphuric Acid for its dissolution for obtaining similar concentrations of Copper. The leaching of the other chemical elements will determine the advantages and disadvantages of each solution. For this purpose, we proceed to describe the concentration in the leachate of the metallic chemical elements that exist in the sample in greater proportions.

The Iron concentration for the four acidic solutions, at different times of the leaching process at ambient temperature and atmospheric pressure, are detailed in Figure 5.

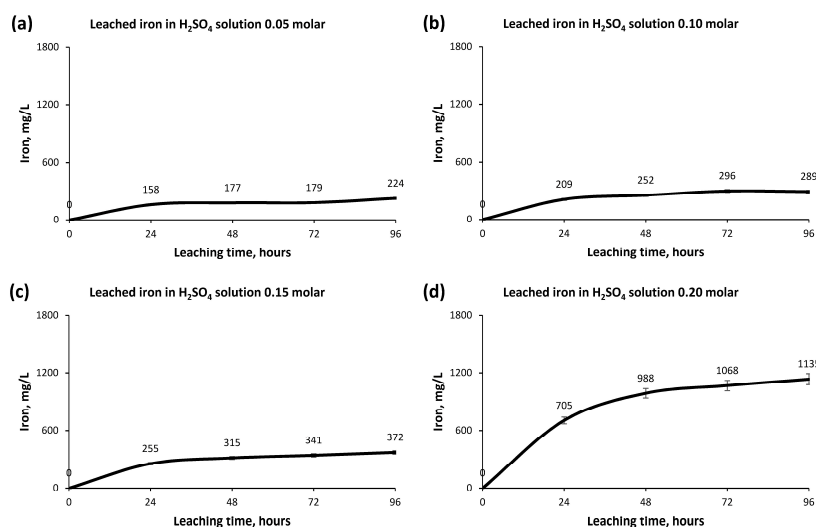


Figure 5. Analysis of the Iron concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H_2SO_4 solution, (b) 0.10 molar H_2SO_4 solution, (c) 0.15 molar H_2SO_4 solution and (d) 0.20 molar H_2SO_4 solution.

The concentrations of Iron in the leachates of the mining waste sample for the four Sulphuric Acid solutions clearly reflect a higher suitability of the 0.20 molar Sulphuric Acid solution, while its concentration in the other solutions is very low. Nevertheless, and based on what has been commented on, the solutions do not present the stabilization of the concentrations of Iron. This fact clearly reflects the need for a longer leaching time, as well as solutions with a greater molarity of Sulphuric Acid for leaching. The maximum percentage of recovery is approximately 36% of the Iron present in the sample.

However, the Iron is not the element that intended to be extracted in this process, focusing the extraction on Copper and secondary elements of greater interest at present. Therefore, it is not recommended to use a higher molarity in the solution of Sulphuric Acid or a longer leaching time, since it would induce a higher extraction of Iron that would complicate the main process of Copper extraction. Therefore, the Iron extraction values for these Sulphuric Acid solutions can be considered acceptable, not being high and not harming the extraction of Copper as the main element.

In turn, the concentration values of Magnesium in the leachates of the different solutions in the process at ambient temperature and atmospheric pressure are detailed in Figure 6.

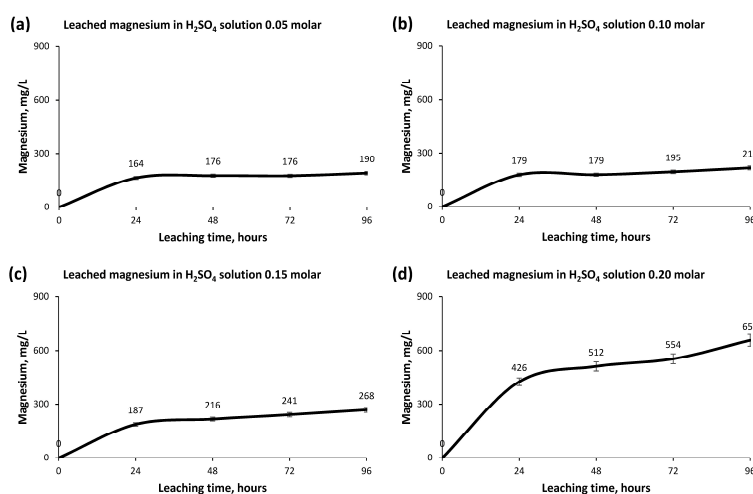


Figure 6. Analysis of the concentration of Magnesium in the leaching process at atmospheric pressure, ambient temperature and in different solutions of Sulphuric Acid: (a) 0.05 molar H_2SO_4 solution, (b) 0.10 molar H_2SO_4 solution, (c) 0.15 molar H_2SO_4 solution and (d) 0.20 molar H_2SO_4 solution.

In the concentration of Magnesium in the different Sulphuric Acid solutions, it can be seen, as in the case of Iron, that the leaching process cannot extract the right percentage of Magnesium. The ascending trend of the 0.20 molar Sulphuric Acid solution clearly reflects this fact. A higher concentration of Sulphuric Acid or a longer leaching time is therefore necessary to exceed the 80% recovery rate of Magnesium. However, the recovery reflects a high value, so Magnesium is not the main element of extraction and to obtain an adequate recovery value, it is not recommended to vary the molarity of the solution nor increase the leaching time, as happens in the case of the Iron. At the same time, the low percentage of recovered Magnesium does not negatively influence the Copper recovery process, this being a hydrometallurgical process which is highly robust and with capacity for the differentiated extraction of the different elements.

The concentration in the Zinc leachates for the different Sulphuric Acid solutions in the process at ambient temperature, atmospheric pressure and different leaching times, are detailed in Figure 7.

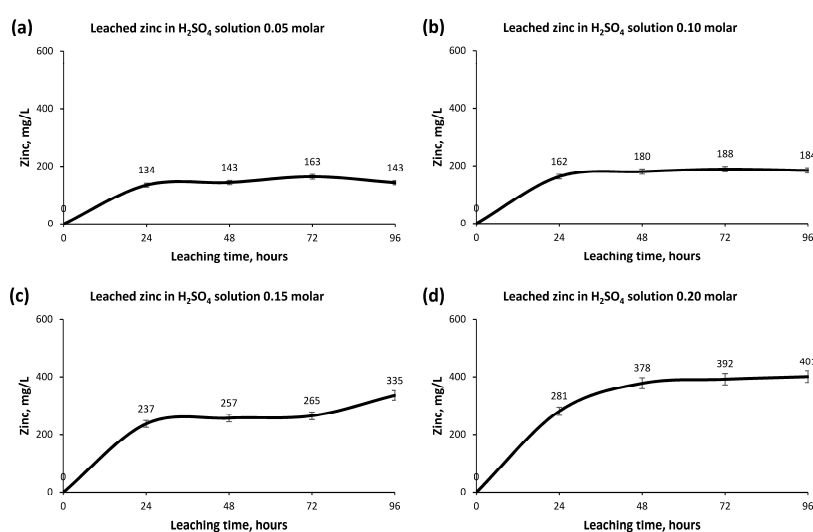


Figure 7. Analysis of Zinc concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H_2SO_4 solution, (b) 0.10 molar H_2SO_4 solution, (c) 0.15 molar H_2SO_4 solution and (d) 0.20 molar H_2SO_4 solution.

In the case of Zinc, behaviors similar to the process of Copper, but even better behaved, occur. The recovery rate of Zinc for the solution of Sulphuric Acid with 0.20 molarity is practically total, obtaining an excellent behavior of the solution. The solutions with smaller molarity of Sulphuric Acid produce a smaller concentration of Zinc, showing better quality results in the 0.15 molar solution than the two solutions of the smaller molarity.

In the solution of Sulphuric Acid with 0.20 molarity, the results of the concentration of Zinc are stabilized, being practically maximum in the first 48 h of the leaching process.

Zinc, in a low proportion in the sample, is a strategic element for obtaining it by hydrometallurgical methods. Therefore, obtaining this secondary element in the leachate makes its later extraction possible, since the cost of the process is assumed by the recovery of Copper and Zinc, which is one more incentive for its economic viability.

Based on the above, the solutions and exposure times are adequate, a higher molarity of Sulphuric Acid or a longer leaching time for the concentration of Zinc not being necessary.

On the other hand, the results of the Manganese concentration in the different Sulphuric Acid solutions and in the different exposure times for the leaching process at ambient temperature and atmospheric pressure are detailed in Figure 8.

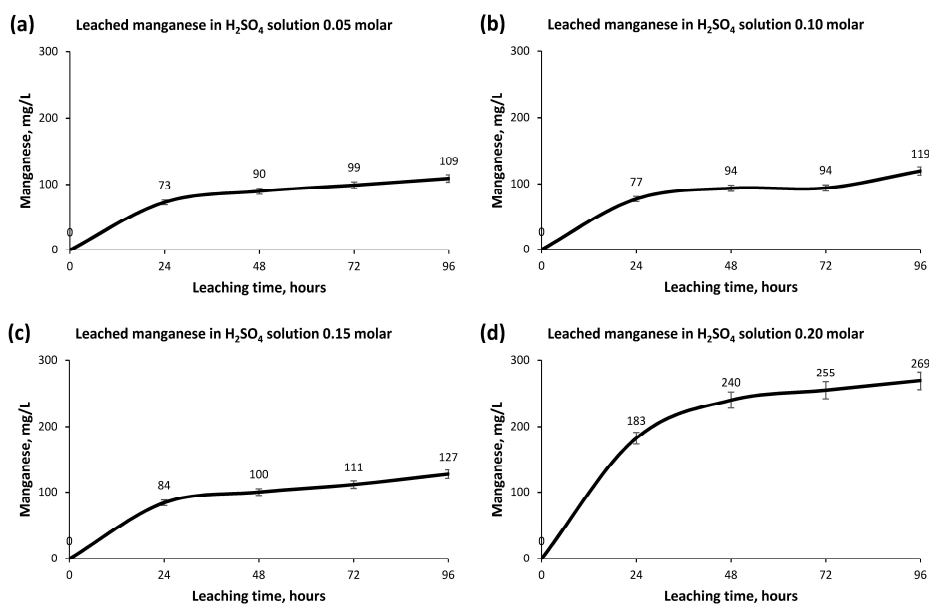


Figure 8. Analysis of the concentration of Manganese in the leaching process at atmospheric pressure, ambient temperature and in different solutions of Sulphuric Acid: (a) 0.05 molar H₂SO₄ solution, (b) 0.10 molar H₂SO₄ solution, (c) 0.15 molar H₂SO₄ solution and (d) 0.20 molar H₂SO₄ solution.

In the case of Manganese, something similar to Magnesium and Iron occurs. There is an inefficiency for the complete extraction of Manganese in the solutions and in the proposed leaching times, the recovery rate being approximately 50%. However, this element is not in the scope of this study and therefore its extraction is unnecessary.

Figure 9 shows the results of the leaching process for Nickel.

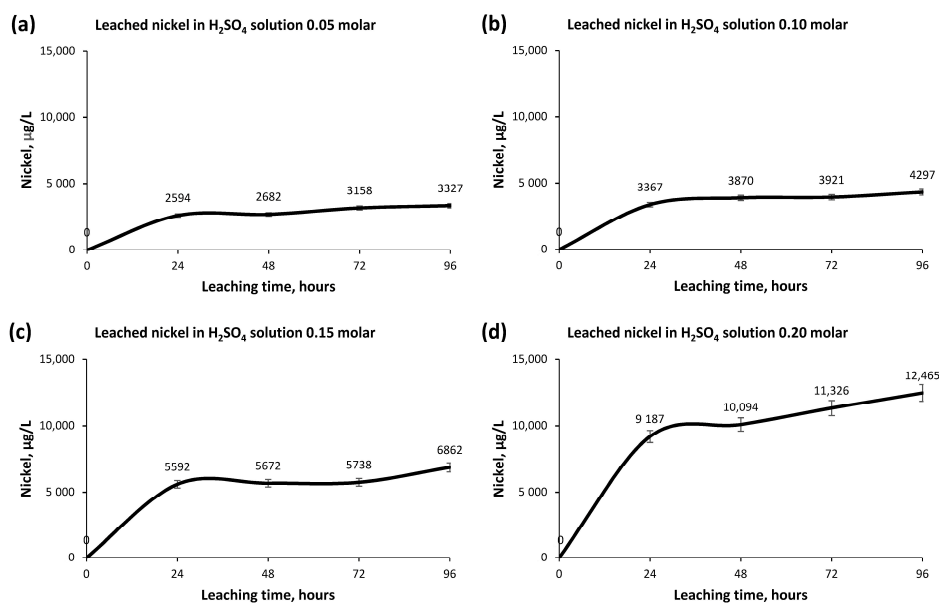


Figure 9. Analysis of the Nickel concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H₂SO₄ solution, (b) 0.10 molar H₂SO₄ solution, (c) 0.15 molar H₂SO₄ solution and (d) 0.20 molar H₂SO₄ solution.

The results of the Nickel concentration in the different solutions and for the different times of the above-mentioned leaching process reflect a similar behavior to Zinc and Copper. The solution of Sulphuric Acid with 0.20 molarity represents the best results, obtaining recovery rates of up to 90%. The other solutions of lower molarity of Sulphuric Acid show incomplete leaching, without the stabilization of concentrations in the stipulated times. The element Nickel is found in low proportion in the sample; however, it is interesting to note a practically full recovery. It is worth noting that it does not influence the Copper extraction process.

The concentrations of Lead in the leachates of the four solutions at different times and in the leaching process are reflected in Figure 10.

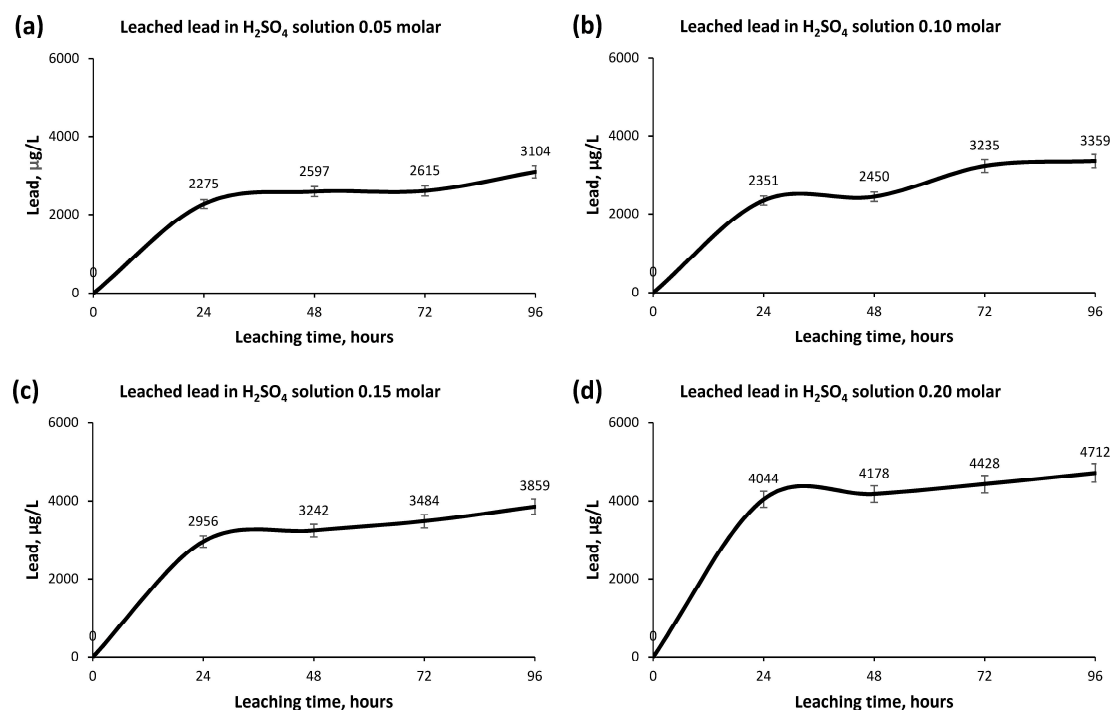


Figure 10. Analysis of Lead concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H_2SO_4 solution, (b) 0.10 molar H_2SO_4 solution, (c) 0.15 molar H_2SO_4 solution and (d) 0.20 molar H_2SO_4 solution.

The concentration of Lead in the leachate of the different solutions presents a minimum recovery rate, so this hydrometallurgical method is not suitable for the recovery of Lead. The low concentration of Lead in the leachates, the problems that it can cause in the extraction of Copper, the reduced percentage in the original sample, as well as the inactivity of Lead before the leaching process, make it possible to affirm that the results are acceptable. This assertion is based on the fact that no unnecessary element is leached in the process that later remains in the leachate and is difficult to treat. This is a good result considering the low interest of Lead in the present study.

On the other hand, the results of the Titanium concentration in the leaching solutions and in the different times, are shown in Figure 11.

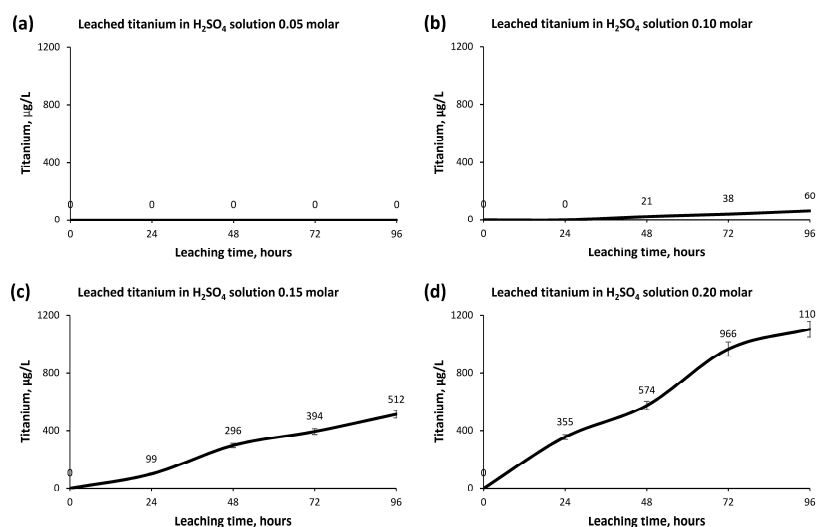


Figure 11. Analysis of the Titanium concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H₂SO₄ solution, (b) 0.10 molar H₂SO₄ solution, (c) 0.15 molar H₂SO₄ solution and (d) 0.20 molar H₂SO₄ solution.

Titanium, as reflected by the x-ray fluorescence test, represents a very low percentage in the mining waste sample and its extraction is not interesting. However, it shows a very interesting behavior to determine by comparison the quality of the Copper leaching process. Unlike the results obtained from the Copper concentrations, the concentrations in the Titanium solutions perfectly show the inactivity of the 0.05 and 0.10 molar Sulphuric Acid solutions. The solutions with molarities 0.15 and 0.20 reflect, on the other hand, the beginning of activity, showing an upward trend without reaching the stabilization in the time and an important difference between the concentrations of the last two solutions. This fact reflects the inadequacy of this leaching process for Titanium, which is not in the scope of the study, and the notable difference with the Copper recovery process is, therefore, determined objectively by the quality of the leaching process for copper recovery from mining waste.

Finally, Figure 12 shows the concentrations of Arsenic in the different solutions and in the different leaching times.

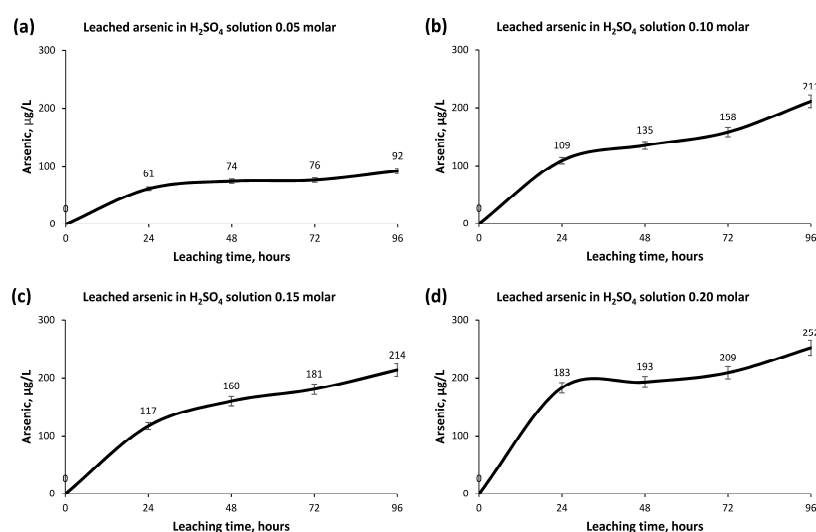


Figure 12. Analysis of Arsenic concentration in the leaching process at atmospheric pressure, ambient temperature and in different Sulphuric Acid solutions: (a) 0.05 molar H₂SO₄ solution, (b) 0.10 molar H₂SO₄ solution, (c) 0.15 molar H₂SO₄ solution and (d) 0.20 molar H₂SO₄ solution.

Arsenic is not an element of interest in recovery by this hydrometallurgical process for different reasons; among them, its low percentage in the sample and the environmental problem that it represents. However, it is an element that seriously damages the pyrometallurgical process and, to a lesser extent, the hydrometallurgical process. Therefore, the low existence of this element in the sample and the low recovery that has been obtained in the leaching, approximately 2%, confirms the quality of the leachate obtained for the extraction of Copper. Furthermore, it confirms the adequacy of the molarity of the Sulphuric Acid in the solutions and the leaching times, since a higher molarity for the extraction of a percentage of Copper would cause an unnecessary leaching of the elements commented as well as of the Arsenic, damaging the process and not obtaining substantial differences in the extraction of Copper due to the increase of the molarity of the Sulphuric Acid solution.

Figure 13 shows the maximum leaching values obtained for the elements detailed above with the 0.20 molar solution of Sulphuric Acid, at ambient temperature and atmospheric pressure.

Chemical leachate

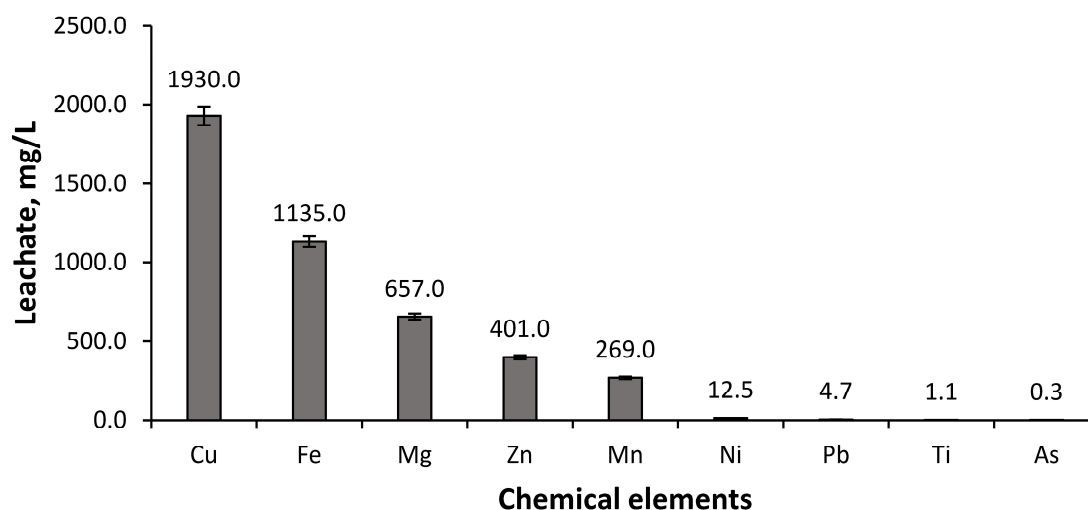


Figure 13. Comparison of the maximum concentration values of the different elements analyzed in the 0.20 molar Sulphuric Acid solution. Leaching process at ambient temperature and atmospheric pressure.

Figure 13 shows how Copper is the element with the highest concentration in the leachate, reaching values of 1.930 ± 0.007 g/L. This value represents an adequate concentration for the viability of the process, causing a rate of recovery of the Copper of the mining waste of approximately 82%. Excellent values if the origin of the raw material, the simplicity of the process and the energy consumption associated with it are taken into account. On the other hand, the element subsequently leached and unavoidable is Iron, in a much lower concentration and with a low recovery rate. This fact is very interesting, since it is not an element of interest for its extraction and its extraction in large proportions can be a problem. The same happens with Magnesium, in much lower concentration than Copper.

The compatibility of the hydrometallurgical process at ambient temperature, atmospheric pressure and low molar acidic media in the extraction of Zinc should be highlighted. The concentration of Zinc in the leachate is even higher than that of Manganese, the latter being an element in greater proportion than Zinc in the sample. The rate of extraction of Zinc from mining waste is almost complete, obtaining low values of concentration in the leachate, but it is interesting to value its extraction as a secondary element.

Contrary to what has been commented on, Lead is not leached in great proportion by the hydrometallurgical process, a fact that benefits the subsequent process of Copper extraction. It is not an element of interest and remains in the waste sample after the leaching process.

Nickel and Titanium appear in very low concentrations in the leachate and, therefore, their percentages are practically negligible. It is worth mentioning the good compatibility of Nickel with the leaching process used, achieving a recovery rate of about 90% and, in turn, achieving a higher concentration in the leachate than Lead and Titanium.

Finally, the low percentage of Arsenic in the leachate should be highlighted. This is an interesting fact since there is a very low recovery rate and it will not condition the hydrometallurgical process, unlike pyrometallurgical techniques in which Arsenic is totally limiting.

4. Conclusions

The partial conclusions obtained from the results of all the tests mentioned in the methodology will be the fundamental basis for the corroboration of the final hypothesis, the leaching of Copper in acidic media, at atmospheric pressure and ambient temperature from mining waste samples for extraction. The importance of using a mining waste, deposited in the vicinity of the seam, without current use and with problems of contamination of underground water and surface water due to its chemical composition, should be highlighted in this study.

The partial conclusions are detailed below.

- The mine waste dump from which the sample was taken for analysis contained mainly granite, Iron Sulphides, Copper Sulphides, Lead Sulphides and, to a lesser proportion, Zinc Sulphides. The Polymetallic Sulphides had been transformed into Oxides by their continuous exposure to the atmospheric conditions and their treatment.
- The chemical composition of the sample under study reflected a low percentage of carbonates and organic matter, with the presence of Copper in a proportion of 4.67%, being a useful sample for the extraction of Copper by hydrometallurgical techniques. There were also percentages of Iron, Lead and Zinc, as well as a low proportion of Arsenic.
- The leaching process was done at ambient temperature so as not to increase the production costs of the process.
- The low molarities of the Sulphuric Acid solutions were selected to avoid subsequent environmental problems with the leachate after the extraction of Copper and elements of interest. In addition, higher molarities of Sulphuric Acid in the solution would have directly caused higher leaching of other elements that are not of interest to extract and would impair the process of extracting Copper from the leachate.
- The particle size between 6 mm and 10 mm of the mine waste sample did not produce sludge at the end of the leaching process for any of the Sulphuric Acid solutions evaluated.
- The leaching times were limited to 96 h, not being necessary longer times as in other hydrometallurgical processes, existing at present in which the leaching time is of weeks and even months.
- The 0.20 molar Sulphuric Acid solution yielded results at 72 h of Copper concentrations of 1.930 ± 0.007 g/L and with recovery rates of approximately 80% of the Copper in the sample. This value is a good result for the subsequent hydrometallurgical stages
- The 0.15 and 0.10 molar Sulphuric Acid solutions give similar results to those of the 0.20 molar Sulphuric Acid solution; nonetheless, which is higher.
- The greatest leaching of Copper occurs in the first 24 h, producing a small increase in concentration afterwards until its stabilization after 72 h.
- Zinc with the 0.20 molar Sulphuric Acid solution has an almost complete recovery rate, obtaining maximum concentrations of 0.401 ± 0.002 g/L. It is therefore a secondary element that can be economically evaluated the interest of its extraction. A similar process occurs with Nickel, but its concentration is very low, so its extraction is of no interest.
- Lead reflected a total incompatibility with the leaching process; therefore, it achieved the objective of not obtaining its leaching and that it remained in the mining sample after the leaching process.

- The other elements, Magnesium, Manganese and Titanium, did not obtain important rates of recovery, a fact that favors the hydrometallurgical process in its later extraction and allows us to recognize the aptitude of the Copper leaching.
- Arsenic, a very harmful element in Copper pyrometallurgical processes and, to a lesser extent, in hydrometallurgical processes, obtained a very low concentration in the leachate and a very low recovery rate. This fact benefits the hydrometallurgical technique.

Based on this, it can be stated that the extraction of Copper from the mining waste in the waste dump belonging to the detailed seam and called “EL COBRE” is feasible, as well as the leaching process in acidic media with low molarity, atmospheric pressure and ambient temperature.

It is worth noting that adequate and comparable Copper leaching values have been obtained to those of other traditional hydrometallurgical processes, through the use of a mining waste (which is not used and which implies environmental pollution) and with a simple, robust and versatile leaching process. Due to these characteristics, this process has a lower economic cost than traditional processes and consumes less energy than other processes, as it is carried out at atmospheric pressure, ambient temperature and in shorter leaching times. At the same time, the low molarity and the absence of sludge after the leaching process make the process more sustainable. These are the competitive advantages of this study compared to pyrometallurgical techniques and other hydrometallurgical processes.

On this basis, it is possible to verify the usefulness of the procedure and of the starting hypotheses for the solution of the problems existing at present in the extraction of Copper, mainly due to the lower grades of the minerals. This is because the lower economic cost of the initial material and low process costs make copper mineral grades viable.

Author Contributions: Conceptualization, F.A.C.-I., F.J.L.d.R., J.M.T.-S. and J.S.-M.; methodology, F.A.C.-I., F.J.L.d.R., J.M.T.-S. and J.S.-M.; software, J.M.T.-S. and J.S.-M.; validation, F.A.C.-I. and F.J.L.d.R.; formal analysis, F.A.C.-I. and F.J.L.d.R.; investigation, J.M.T.-S. and J.S.-M.; resources, F.A.C.-I.; data curation, F.J.L.d.R.; 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.

Acknowledgments: 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

1. Li, L.; Pan, D.; Li, B.; Wu, Y.; Wang, H.; Gu, Y.; Zuo, T. Patterns and challenges in the copper industry in China. *Resour. Conserv. Recycl.* **2017**, *127*, 1–7. [CrossRef]
2. Wang, M.; Chen, W.; Zhou, Y.; Li, X. Assessment of potential copper scrap in China and policy recommendation. *Resour. Policy* **2017**, *52*, 235–244. [CrossRef]
3. Wang, H.T.; Liu, Y.; Gong, X.Z.; Wang, Z.H.; Gao, F.; Nie, Z.R. Life Cycle Assessment of Metallic Copper Produced by the Pyrometallurgical Technology of China. *Mater. Sci. Forum* **2015**, *814*, 559–563. [CrossRef]
4. Bonnin, M.; Azzaro-Pantel, C.; Domenech, S.; Villeneuve, J. Multicriteria optimization of copper scrap management strategy. *Resour. Conserv. Recycl.* **2015**, *99*, 48–62. [CrossRef]
5. Shuva, M.A.H.; Rhamdhani, M.A.; Brooks, G.A.; Masood, S.; Reuter, M.A. Thermodynamics data of valuable elements relevant to e-waste processing through primary and secondary copper production: A review. *J. Clean. Prod.* **2016**, *131*, 795–809. [CrossRef]
6. Copper: World Mine Production, By Country. Available online: https://www.indexmundi.com/en/commodities/minerals/copper/copper_t20.html (accessed on 19 May 2020).
7. Kowalczyk, P.; Bouzahzah, H.; Kleiv, R.; Aasly, K. Simultaneous Leaching of Seafloor Massive Sulfides and Polymetallic Nodules. *Minerals* **2019**, *9*, 482. [CrossRef]
8. Watling, H.R. Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate-chloride and sulfate-nitrate process options. *Hydrometallurgy* **2013**, *140*, 163–180. [CrossRef]

9. Meshram, P.; Prakash, U.; Bhagat, L.; Abhilash; Zhao, H.; van Hullebusch, E.D. Processing of Waste Copper Converter Slag Using Organic Acids for Extraction of Copper, Nickel, and Cobalt. *Minerals* **2020**, *10*, 290. [[CrossRef](#)]
10. Hernández, P.C.; Dupont, J.; Herreros, O.O.; Jimenez, Y.P.; Torres, C.M. Accelerating copper leaching from sulfide ores in acid-nitrate-chloride media using agglomeration and curing as pretreatment. *Minerals* **2019**, *9*, 250. [[CrossRef](#)]
11. Hernández, P.; Taboada, M.; Herreros, O.; Graber, T.; Ghorbani, Y. Leaching of Chalcopyrite in Acidified Nitrate Using Seawater-Based Media. *Minerals* **2018**, *8*, 238. [[CrossRef](#)]
12. Chen, J.; Wang, Z.; Wu, Y.; Li, L.; Li, B.; Pan, D.; Zuo, T. Environmental benefits of secondary copper from primary copper based on life cycle assessment in China. *Resour. Conserv. Recycl.* **2019**, *146*, 35–44. [[CrossRef](#)]
13. Jones, D.J. CESL Copper Process. In Proceedings of the Alta Copper Hydrometallurgy Forum, Brisbane, Australia, 14–15 October 1996.
14. Watling, H.R.; Elliot, A.D.; Maley, M.; van Bronswijk, W.; Hunter, C. Leaching of a low-grade, copper-nickel sulfide ore. 1. Key parameters impacting on Cu recovery during column bioleaching. *Hydrometallurgy* **2009**, *97*, 204–212. [[CrossRef](#)]
15. Wang, S. Copper leaching from chalcopyrite concentrates. *JOM* **2005**, *57*, 48–51. [[CrossRef](#)]
16. Dreisinger, D. Copper leaching from primary sulfides: Options for biological and chemical extraction of copper. *Hydrometallurgy* **2006**, *83*, 10–20. [[CrossRef](#)]
17. van Staden, P.J. The Mintek/Bactech copper bioleach process. In Proceedings of the ALTA Copper Hydrometallurgy Forum, Brisbane, Australia, 19–21 October 1998.
18. Gericke, M.; Govender, Y.; Pinches, A. Tank bioleaching of low-grade chalcopyrite concentrates using redox control. *Hydrometallurgy* **2010**, *104*, 414–419. [[CrossRef](#)]
19. Hourn, M.; Halbe, D. The Nena Tech Process: Results on Frieda River copper gold concentrates. In Proceedings of the International Conference of Randol Copper Hydromet Roundtable 1999, Phoenix, AZ, USA, 10–13 October 1999; pp. 97–102.
20. Hourn, M.M.; Turner, D.W.; Holzberger, I.R. Atmospheric Mineral Leaching Process. U.S. Patent 5,993,635, 30 November 1999.
21. Cerda, C.; Taboada, M.; Jamett, N.; Ghorbani, Y.; Hernández, P. Effect of Pretreatment on Leaching Primary Copper Sulfide in Acid-Chloride Media. *Minerals* **2017**, *8*, 1. [[CrossRef](#)]
22. Arroyo, F.; Fernández-Pereira, C.; Bermejo, P. Demonstration Plant Equipment Design and Scale-Up from Pilot Plant of a Leaching and Solvent Extraction Process. *Minerals* **2015**, *5*, 298–313. [[CrossRef](#)]
23. Peacey, J.; Guo, X.J.; Robles, E. Copper hydrometallurgy—Current status, preliminary economics, future direction and positioning versus smelting. *Trans. Nonferrous Met. Soc. China (Engl. Ed.)* **2004**, *14*, 560–568.



© 2020 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 (<http://creativecommons.org/licenses/by/4.0/>).