

Article

Recovery of Tetrahedrite from Mining Waste in Spain

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Abstract

The present study is part of the Horizon Europe-START project, which aims to recover tetrahedrite-group minerals present in mine dumps to be used as raw materials for the manufacture of thermoelectric devices. The aim of this work is to identify the mining waste facilities selected in Spain for the recovery of tetrahedrite and to outline the mineral processing operations performed on samples from each site to separate and concentrate this mineral. Ore deposits across Spain were selected based on the potential presence of tetrahedrite in their mining waste. A total of five deposits have been sampled, at which subsequent mineral separation and concentration tests have been conducted. A separation flowsheet is proposed in order to extract a high-purity tetrahedrite concentrate. Experimental results indicate two distinct options for separation approaches, depending on a key parameter that proves decisive in the processing of this mineral, which is whether the mineral paragenesis includes siderite. This study has demonstrated the technical feasibility of concentrating minerals of the tetrahedrite group through simple, cost-effective physical separation techniques—specifically magnetic and gravity separation—where the liberation size of the tetrahedrite exceeds 0.063 mm.

Keywords: tetrahedrite; circular economy; mining wastes; thermoelectric materials



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1. Introduction

Global energy demand has increased exponentially, especially in recent decades [1–3]. In addition, it is estimated that two-thirds of the total energy generated worldwide is lost in the form of waste heat [4]. Recovering this wasted energy is therefore essential to achieve greater energy efficiency. Thermoelectric generators can provide a solution to this problem, as they can convert waste heat into electrical energy in a direct and reversible manner. However, a number of challenges need to be overcome before this technology can become widely available, including its low efficiency, the high cost of raw materials needed to manufacture these devices, and their environmental sustainability.

Minerals of the tetrahedrite group comprise a suite of sulfosalts commonly found in hydrothermal deposits. They represent a significant ore of copper, along with other elements such as antimony, arsenic, and silver. These minerals exhibit excellent thermoelectric properties, making them suitable for the manufacture of devices that harness residual heat generated during different industrial processes [5,6]. Furthermore, when

combined with synthetic tetrahedrite, thermoelectric properties are enhanced [7]. These attributes have generated much interest in the last decade [5,6,8], driving, among others, the development of an EU-funded project titled “Sustainable Energy Harvesting Systems Based on Innovative Mine Waste Recycling” (acronym: START). The project aims to recover tetrahedrite from abandoned mine waste dumps to evaluate its potential in the production of thermoelectric devices.

The primary advantage of valorising such mining residues lies in the fact that the material has already been extracted and partially crushed, thereby significantly reducing energy consumption. It is crucial to ensure that the recovery process of tetrahedrite is low-cost in terms of operational expenditure to make the valorisation economically feasible. Another benefit stems from the relative ease of obtaining permits for the secondary utilisation of waste materials, in contrast to the complexities of licensing new geological mining operations. Besides, these residues often contain environmentally hazardous elements such as sulphur and arsenic. Recovering these waste materials will contribute to the removal of such pollutants from the environment.

It is important to note that the European Commission, through initiatives like the European Green Deal and the twin ecological and digital transitions, aims for a climate-neutral Europe by 2050. Mining wastes could serve as a valuable secondary source of critical and strategic materials. Recovering such wastes aligns with the EU's Circular Economy Action Plan (COM(2020) 98) [9] and the Critical Raw Materials Act (REGULATION (EU) 2024/1252) [10], which encourages resource recovery while mitigating environmental risks. In this way, the START project will contribute to the achievement of energy neutrality and economic circularity, which are essential today. Specifically, the aim of this study is to identify the mining waste facilities selected in Spain for the recovery of tetrahedrite and to outline the mineral processing operations performed on samples from each site to separate and concentrate this mineral.

2. Materials and Methods

2.1. Selection of Tetrahedrite in Representative Locations

Spain is distinguished by its considerable lithological diversity and complex geology—factors which, combined with a long-standing and widespread mining tradition, significantly increase the likelihood of finding tetrahedrite in abandoned mine waste rock dumps.

A bibliographic survey was conducted, complemented by the integration of geochemical and mineralogical data provided by the Spanish Geological Survey (IGME-CSIC), derived from both the Mineral Resources Database (BDMIN) [11] and the National Inventory of Tailings and Waste Dumps [12]. This resulted in a preliminary list of potential areas, identifying around 250 sites with documented tetrahedrite occurrences.

From this initial set, only those locations where tetrahedrite constitutes the principal mineral phase were selected, narrowing the pool to 50 sites. After this selection based uniquely on bibliographic data, further consideration of factors such as tetrahedrite content, grain size, and dump volume led to a finer selection of 22 zones distributed across the territory of Spain. These are located in the Cantabrian Zone (4 mines), the Asturian-Western Leonese Zone (3 mines), the Central Iberian Zone (1 mine), the Ossa Morena Zone (2 mines), the South Portuguese Zone (3 mines), the Pyrenees (2 mines), the Iberian Range (6 mines), and the Betic Cordillera (1 mine).

Nevertheless, the available information required field validation, prompting on-site verification work in the selected areas. After sampling campaigns and in situ assessment of dump volume and grain size, five waste rock dumps were ultimately chosen for further study: El Coriellu and Delfina Mines (Asturias), Santísima Trinidad Mine, in Torres de

Albarracín (Teruel), La Profunda Mine in Cármenes (León), and El Vagón Mine, Lanteira Group (Granada). The different symbols in Figure 1 represent the location of the five facilities finally chosen for this study.

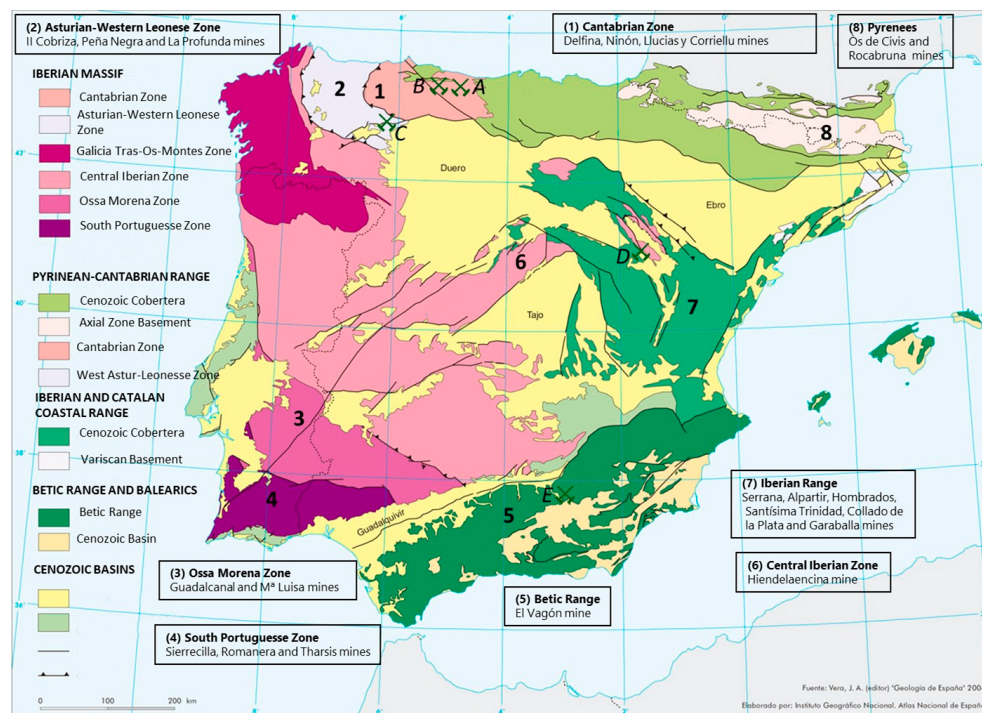


Figure 1. Schematic map showing the final selection of facilities for the study: **A:** Delfina Mine, **B:** El Coriellu Mine, **C:** La Profunda Mine, **D:** Santísima Trinidad Mine, and **E:** El Vagón Mine (Lanteira Group) [13].

The samples in these selected dumps were taken in such a way that, on the one hand, they contained enough tetrahedrite to obtain a concentrate in the laboratory, and on the other hand, they were as representative as possible of each of the dumps.

For this purpose, a 1 m × 1 m surface grid was made in which the fragments where mineralisation was observed were collected by hand. Thus, a composite sample of fragments with mineralisation was obtained from the entire dump. Since prior sorting was conducted during sampling, the samples obtained for the tests did not have the same weight.

2.2. Description of the Ores Selected for the Study

2.2.1. Delfina Mine

Located near Ortiguero, in the municipality of Cabrales (Asturias) (Figure 2), this is a low-temperature hydrothermal mineralisation hosted in Carboniferous limestones of the Picos de Europa Formation.

The ore, comprising copper sulphides and sulfosalts, occurs in narrow subvertical veins and veinlets, as well as irregular masses that fill karstic cavities [14]. It is altered in most parts. Primary minerals include tennantite and chalcopyrite, with minor pyrite. Secondary enrichment zones contain chalcocite, covellite, bornite, digenite, and talnakhite. The gangue is predominantly calcium carbonate, with dolomite and quartz as accessories.

Alteration minerals are mostly arsenates—typical of tennantite-rich systems—including clinoclase, conichalcite, pharmacosiderite, sabellite, theisite, tyrolite, and zalesiite [15]. Copper carbonates are also present, with azurite being more abundant than malachite.



Figure 2. Remains of the abandoned Delfina Mine, with the waste dump at the bottom.

2.2.2. El Coriellu Mine

Situated approximately 2 km south of Llerandi, in the municipality of Parres (Asturias), this is another low-temperature hydrothermal mineralisation within Carboniferous limestones of the Barcaliente Formation (Peñamayor Limestone).

The ore is mainly tetrahedrite (Figure 3), with chalcopyrite only occurring rarely. It is present in small quartz veins, where tetrahedrite occupies the central zone in centimetre-scale veins, sometimes anastomosing and filling karstic cavities. Secondary minerals include copper carbonates, primarily azurite. Tetrahedrite crystals sometimes display a thin patina of malachite alteration [16].



Figure 3. Specimen of tetrahedrite from the Geominero Museum collection (IGME-CSIC).

2.2.3. Santísima Trinidad Mine

This site is the most significant among a group of mines located north of Torres de Albarracín (Teruel). The mineralisation is hosted in Ordovician quartzites (Tremedal Quartzites) and consists of a quartz vein flanked by siderite lenses. Tetrahedrite is only present as fine grains disseminated within the siderite.

The primary ore is galena, with tetrahedrite as an accessory phase and chalcopyrite only occasionally present. The ores are minimally altered, and secondary minerals (azurite and malachite) are rare [17].

2.2.4. El Vagón Mine (Lanteira Group)

This mine lies on the northern slope of the Sierra Nevada, above the village of Lanteira (Granada). The studied area is part of a thick series of garnet-bearing black

schists interbedded with quartzites, which belong to the Carboniferous-aged Nevado-Filábride Complex.

This unit is cross-cut by a series of siderite veins oriented N10 to N20E, which contain, in some places, appreciable but irregularly distributed quantities of complex sulphides. The veins are typically 10–20 cm thick, but locally widen up to 1 m.

Minerals identified include siderite, chalcopyrite, quartz, pyrite, arsenopyrite, galena, and tetrahedrite [18].

2.2.5. La Profunda Mine

Located 2.5 km NW of Cármenes (León), this is the most prominent mine among several mining works associated with hydrothermal activity along a fault that mineralises Carboniferous limestones (Valdeteja Formation), particularly at the top of the so-called Montaña Limestone [19]. Originally mined for copper, the deposit also contains minor concentrations of cobalt, nickel, and uranium.

Primary minerals include chalcopyrite, bornite, tennantite, villamaninite, and uraninite. Some magnetite was also identified during mineral concentration. The sulphides are subject to supergene alteration, resulting in secondary chalcocite, arsenates, and carbonates, including erythrite, tyrolite, zeunerite, pharmacosiderite, conichalcite, annabergite, and azurite [20,21].

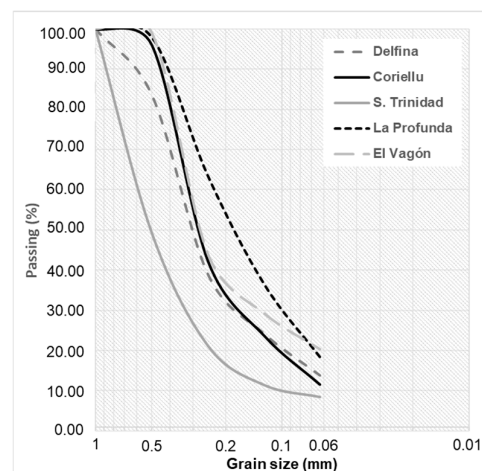
2.3. Sample Preparation: Grinding and Sieving

The first step in sample preparation consisted of crushing the material to below 1 mm (Figure 4a). Any fraction exceeding 1 mm was re-crushed and sieved until the entire sample passed below the 1 mm threshold.

The samples underwent a multi-stage comminution process at the IGME laboratory: First, a primary crushing step was carried out using a RETSCH BB250 jaw crusher (Biometa, Haan, Germany), with a feed opening of 120 × 90 mm and an output size of approximately 0.5 cm. If any material remained above 0.5 cm after this stage, a secondary crushing step was performed using a HUMBOLDT WEDAG (Cologne, Germany) roller mill to reduce particle size to below 0.5 cm. In some cases, additional fine grinding was applied using a TEMA mill–SIEBTECHNIK (TEMA Maquinaria S. A., Mülheim, Germany) equipped with a steel grinding bowl, achieving particle sizes below 0.074 mm. The final particle size in this step depended on the milling time.



(a)



(b)

Figure 4. (a) Crushed sample (Delfina Mine) for its subsequent grinding. (b) Granulometric curve of the ground and sieved samples to perform the assays.

Subsequently, samples were subjected to sieving in a vibrating sieve stack for an average of 8 min. The sieving process employed mesh sizes of 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, and 0.063 mm.

Particular care was taken to avoid over-crushing, which would result in the generation of excessive fines (<0.063 mm). However, as observed in Figure 4b, this fine fraction was around 10%–20%. Such fine particles hinder gravity and magnetic concentration processes, or otherwise require the use of costlier and less sustainable alternatives (such as flotation and/or leaching). There are gravity concentration devices capable of operating at particle sizes below 50 μm [22], such as centrifugal concentrators (e.g., multi-gravity separators, Falcon, Knelson), which apply centrifugal forces to enhance separation. These devices are generally difficult to control, and their recovery rates are often quite low. A major challenge in applying this technique to the current samples is the presence of several heavy minerals whose behaviour—particularly in the fine size fractions—would be very similar, making their separation highly complex. The treatment of this fraction remains, therefore, out of the scope of the present work.

Using a binocular microscope, the grain size at which liberation occurs was determined (Figure 5). Systematically, a sample of each of the particle size fractions at which the samples were sieved was passed through this microscope to assess the degree of liberation of the grains. It was observed that up to the 0.5 mm size, the tetrahedrite was liberated from other minerals, but at larger sizes, the samples showed a higher proportion of mixed grains.

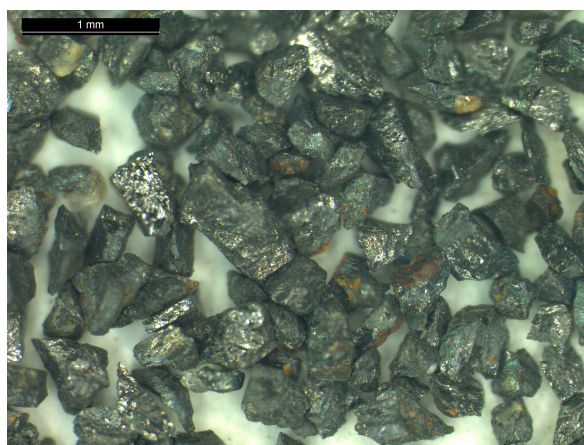


Figure 5. Example of liberated grains through a binocular microscope in Profunda Mine (scale bar in the upper left-hand corner).

3. Results

Samples from the five previously described deposits have been tested. The objective of this phase of the project was to select as much tetrahedrite as possible for subsequent characterisation and determination of its thermoelectric properties. For this purpose, sufficient material was selected in the field so that separation and concentration tests of tetrahedrite could be carried out.

3.1. Laboratory-Scale Concentration Tests of Tetrahedrite

The treatment process followed for the concentration of tetrahedrite at the laboratory level in each of the samples collected at the different locations was as follows:

Delfina Mine (Ortiguero, Asturias): A 25.2 kg sample was taken. It was ground below 1 mm and sieved into the different granulometric fractions indicated in Section 2.3. Then, in order to separate the tetrahedrite together with other denser minerals, each fraction was treated by gravimetric concentration on a Wilfley shaking table. The fraction smaller than

0.063 mm was not tested gravimetrically, as this type of separation is not feasible at such fine sizes. With this gravimetric concentration stage, as it is a wet process, a desliming of the sample is achieved, simultaneously with the pre-concentration of the dense minerals (where the tetrahedrite is incorporated). The low-density fraction is discarded, which corresponds to gangue minerals, mainly calcite, quartz from the host rock, and other minerals such as tyrolite, which was very abundant in this sample.

Before drying the sample in the stove, the concentrates obtained were washed with alcohol (70°) to avoid the formation of iron oxides that act as cement, forming aggregates that make subsequent separations difficult. Subsequently, a high-intensity magnetic separation was carried out with a Frantz isodynamic electromagnet. At an intensity of 1 A, the tetrahedrite, together with other minor sulphides, was separated from most of the diamagnetic minerals, which in this case are quartz, calcite, and other carbonates, still remaining, and copper arsenates. The final concentration obtained from the sample was 4.76%.

In order to verify that the sample was well concentrated, a qualitative analysis was carried out by X-ray diffraction at the IGME laboratory (Figure 6). In this sample, minerals detected were tetrahedrite, quartz, azurite, dolomite, ankerite, and pyrrhotite.

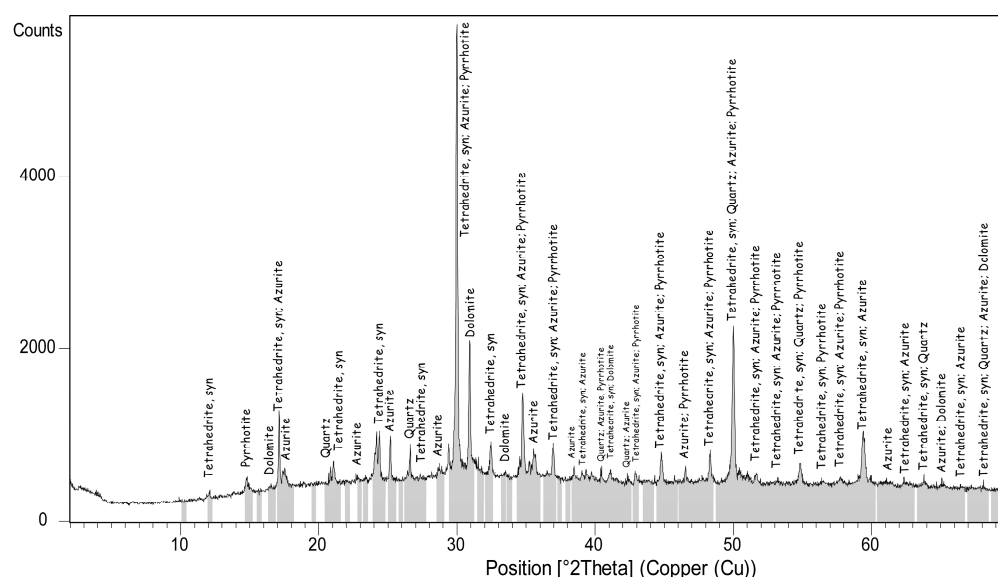


Figure 6. Diffractogram of a sample corresponding to a concentrate of Delfina Mine.

El Coriellu Mine (Llerandi, Asturias): The sample collected (50.5 kg) was characterised after grinding and sieving, revealing a maximum liberation size of 0.5 mm, quite coarse, which favours the application of gravimetric and magnetic concentration processes. Granulometric fractions larger than 0.063 mm were tested separately by wet gravimetric pre-concentration on the Wilfley shaking table, where the gangue minerals (quartz and carbonates) were separated from the tetrahedrite and other dense minerals. After washing with alcohol and drying of the concentrated sample, the dense fraction was separated in the Frantz electromagnetic separator at 0.7 A, and the final concentrate was obtained. Figure 7 shows an example of the concentrate obtained in one round for the granulometric fraction between 0.25 mm and 0.5 mm. In this case, the final concentration was 9.89% of the total weight of the treated material. This value is very similar to the proportion of concentrate obtained from the whole sample, which was 10%. Here, minerals detected in samples by XRD were tetrahedrite, quartz, azurite, and malachite.

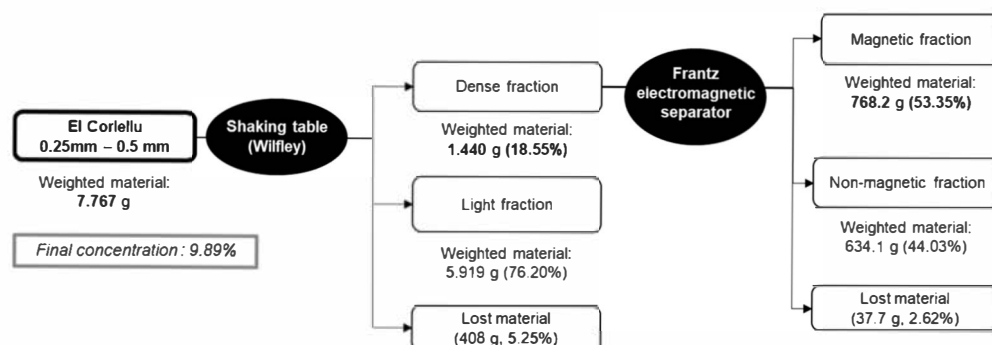


Figure 7. Schematic diagram of the concentration process in one round of the 0.25–0.5 mm granulometric fraction.

Santísima Trinidad Mine, Torres de Albarracín (Teruel): Here, a sample of 38.4 kg was taken from the dump. This sample contains siderite as the main mineral, with contents in the sample selected in the field of more than 80%. Siderite is accompanied by tetrahedrite, galena, and quartz. Once ground and sieved, it was found that the liberation size is also 0.5 mm in this case. It was tested in a first stage on a shaking table, following the same procedure as in the other samples.

However, this treatment did not give the expected results due to the high siderite content that hindered the selectivity and differentiation of the tetrahedrite in the exit zones of the shaking table. The procedure that was finally followed is shown in Figure 8.

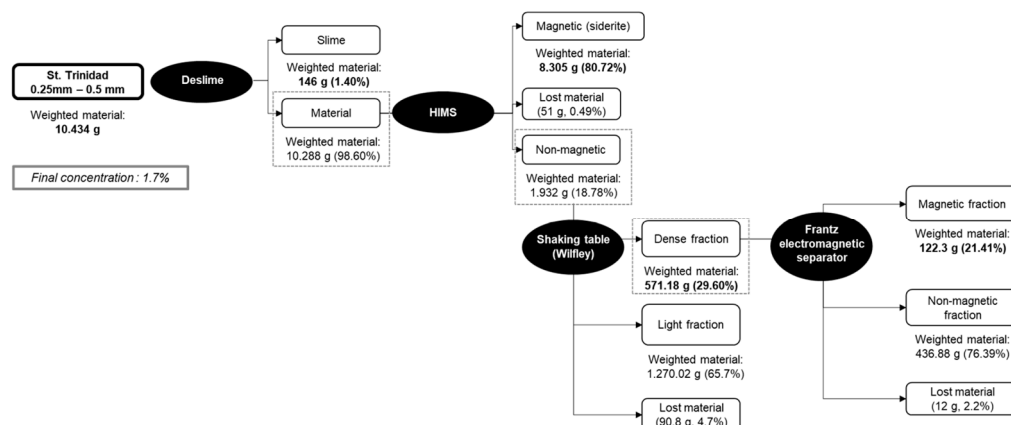


Figure 8. Schematic diagram of the concentration procedure followed for the Santísima Trinidad sample. This is an example of a complete round concentrating a part of the 0.25–0.5 mm fraction.

As an alternative to the gravimetric pre-concentration process and after desliming, a high-intensity magnetic separation process (HIMS) was applied directly to each of the granulometric fractions with a permanent rare earth magnet (field of 10.000 Gauss = 1 Tesla) (Figure 9a).

In this case, both siderite and tetrahedrite are paramagnetic, but undoubtedly, siderite has a higher magnetic susceptibility, so at this intensity, siderite has been mostly concentrated in the magnetic fraction, while tetrahedrite has been mainly separated in the non-magnetic fraction together with other minerals such as galena, as well as gangue minerals, such as quartz, which is also present in high proportion. The magnetic fraction was separated in several rounds (four in total) in order to recover some more tetrahedrite remaining in this fraction and increase its recovery. Figure 9b shows the difference between the samples obtained in the magnetic and non-magnetic fractions in the rare earth magnet for sizes between 1 mm and 0.5 mm. The non-magnetic fraction includes tetrahedrite together with quartz and galena.



Figure 9. Separation by HIMS of the Santísima Trinidad sample. (a) Rare earth permanent magnet high-intensity magnetic separator and (b) fractions obtained from HIMS with rare earth permanent magnet at 0.5–1 mm (magnetic-siderite fraction, right vs. non-magnetic fraction, left).

Subsequently, the non-magnetic fraction was subjected to gravimetric separation on a Wilfley table (Figure 10). In this way, it was possible to separate a large part of the quartz present in this fraction and some remaining siderite. Nevertheless, if the Taggart criterion is applied, which is used to calculate if separation between two minerals is possible, low relative density difference values of 1.5 or 1.8 are observed between galena and tetrahedrite, depending on which density is taken for tetrahedrite. This indicates a difficult separation between tetrahedrite and galena. Such separation would only be possible at coarse sizes (above the tetrahedrite liberation size of 0.5 mm), or the gravimetric pre-concentrate of tetrahedrite and galena could be regrinded below the liberation size and reprocessed again on the table. This latter treatment option would undoubtedly increase the costs. Figure 10 clearly shows the separation of the denser minerals (tetrahedrite and some galena) on the left, from the gangue minerals (quartz and siderite). Although in this study, siderite is considered as tailings, in this case of the Torres de Albarracín, it could become a by-product for the iron and steel sector due to its presence in large quantities.

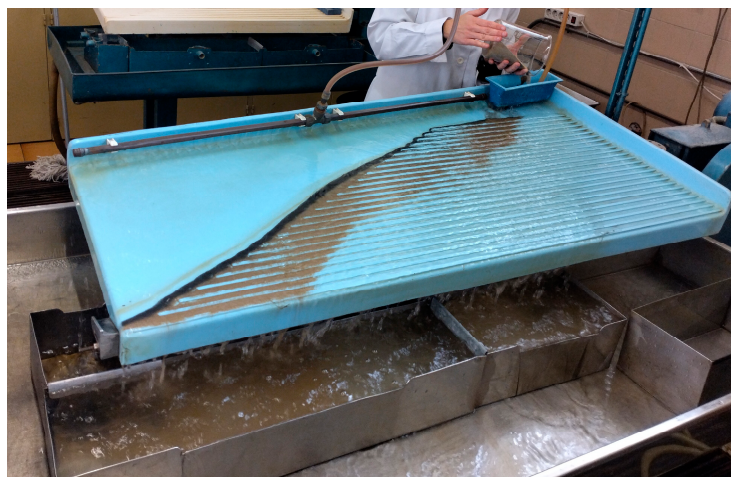


Figure 10. Wilfley shaking table at the laboratories of the Geological Survey of Spain (IGME-CSIC).

Finally, it was again decided to treat the dense sample of the non-magnetic band from the shaking table, already free of quartz and the rest of the siderite, in a Frantz electromagnet of high intensity (0.7 A). At this stage, it was possible to separate the diamagnetic galena,

i.e., non-magnetic, from the paramagnetic tetrahedrite. The concentrate recovered from the whole sample was around 1%. The round concentrated in Figure 8 gave better results, probably due to the suitability of the grain size. Samples of the final concentrate analysed by XRD showed significant mineral contents of tetrahedrite, along with quartz, galena, and bournonite.

In this study, the concentration of the siderite has obtained a high recovery in all the granulometric fractions in the high-intensity magnetic separation (HIMS). However, in order to analyse its possible applications in the iron and steel sector, it would be necessary to study in more detail its possible metallurgical recovery in terms of iron content and impurities. It should be noted, however, that the sample selected in the field is not fully representative, as it would have to be a sample obtained as a mixture of samples taken from different points and using an appropriate sampling methodology to improve representativeness.

La Profunda Mine (Cármenes, León): A sample of about 12 kg was taken. After grinding and sieving into the different particle size fractions, the sample collected was studied, and the tetrahedrite ore was found again to have a liberation size of 0.5 mm. The fractions > 0.063 mm were treated on the Wilfley gravimetric concentration table in order to obtain a dense pre-concentrate containing tetrahedrite that is separated from the lighter fraction containing quartz and carbonates. In this case, a small concentration of magnetite was detected, which had to be extracted using a permanent ferrite magnet. Finally, after washing with alcohol and stove drying, the tetrahedrite concentrate was obtained by separating this mineral from other non-magnetic sulphides with the Frantz magnetic separator at 0.7 A. In this case, the material concentrated was 13% of the collected sample. XRD analyses detected minerals such as tennantite, chalcopyrite, malachite, dolomite/ankerite, quartz, tetrahedrite, brochantite, or azurite.

El Vagón Mine in Lanteira (Granada): Here, the primary mineralisation consists mainly of copper sulphides and sulphosalts, where chalcopyrite and tetrahedrite (which is always associated with siderite) predominate. In this case, the test was carried out on a small sample of 3.7 kg. The same separation process was followed as in the sample from the Santísima Trinidad Mine, as the paragenesis includes siderite. However, the liberation size of this sample turned out to be much smaller, as well as the lower amount of tetrahedrite, and a higher sulphide content, which made concentration difficult. High-intensity magnetic separation with permanent magnets did not give good results, even though this procedure is the most suitable. The recovery in the different granulometric fractions did not reach 0.5% of concentrate with respect to the total of the sample. Therefore, the tests on this sample were cancelled, as this procedure was not suitable for this type of paragenesis and grain size. In this case, different separation treatments, such as flotation, should be applied.

3.2. Characterisation of the Obtained Tetrahedrite

As a final step of the work, the tetrahedrite from the deposits that produced the best results in the separation tests was characterised. The final objective of obtaining this tetrahedrite is its use in thermoelectric devices. Although these devices are created by doping the natural mineral, the initial chemical composition can influence the final properties of the material [23,24].

Quantitative chemical analyses were carried out using a JEOL JXA iHP-200F electron microprobe (JEOL Ltd. Tokyo, Japan) at the National Centre for Electron Microscopy of Madrid, Spain. Experimental conditions were as follows: wavelength-dispersive spectroscopy mode, 20 kV, beam current 50 nA, beam diameter 1 micra. Standards (element, emission line) were as follows: AsGa TAPL (AsL α), galena PETL (SK α), Ag PETL (AgL α), Sb PETL (SbL α), Fe LIFL (FeK α), Cu LIFL (CuK α), and gannita LIFL (ZnK α). Matrix correction by ZAF software (version 2.8.0.9) was applied to the data.

Five analyses have been performed for each mineral deposit. In the case of Delfina Mine, two compositional ranges have been observed, leading to the identification of two distinct groups of analyses (Delfina 1 and Delfina 2). Chemical data are given in Table 1.

The chemical formula was calculated assuming $S = 13$ apfu, and the specimens were classified based on [25]. The low silver concentration was assigned to the M1 site, and it has been assumed that no vacancies occur at M(2), M(1), and X(3). The samples are characterised by the following chemical formulas:

- Delfina 1: $(Cu_{5.87}Ag_{0.13})_{\Sigma 6.00} [Cu_{4.00}(Fe_{1.04}Cu_{0.78}Zn_{0.24})_{\Sigma 2.06}] (Sb_{2.29}As_{1.68})_{\Sigma 3.97}S_{13}$. It corresponds to tetrahedrite-(Fe).
- Delfina 2: $(Cu_{5.73}Ag_{0.27})_{\Sigma 6.00} [Cu_{4.00}(Cu_{0.92}Fe_{0.85}Zn_{0.52})_{\Sigma 2.29}] (Sb_{3.55}As_{0.55})_{\Sigma 4.10}S_{13}$. It corresponds to tetrahedrite-(Cu).
- El Coriellu: $(Cu_{5.99}Ag_{0.01})_{\Sigma 6.00} [Cu_{4.00}(Cu_{0.83}Zn_{0.81}Fe_{0.62})_{\Sigma 2.26}] (Sb_{3.44}As_{0.66})_{\Sigma 4.10}S_{13}$. It corresponds to tetrahedrite-(Cu).
- Santísima Trinidad (S.T.): $(Cu_{5.67}Ag_{0.33})_{\Sigma 6.00} [Cu_{4.00}(Fe_{1.37}Zn_{0.67}Cu_{0.03})_{\Sigma 2.07}] (Sb_{3.59}As_{0.53})_{\Sigma 4.12}S_{13}$. It corresponds to tetrahedrite-(Fe).
- La Profunda: $Cu_6[Cu_{4.00}(Fe_{0.83}Cu_{0.72}Zn_{0.64})_{\Sigma 2.19}] As_{3.84}S_{13}$. It corresponds to tennantite-(Fe).

Table 1. Mean composition obtained from electron microprobe analyses (wt.%).

	Delfina 1	Delfina 2	El Coriellu	S. T.	La Profunda
Cu	41.50	38.70	41.45	37.46	45.68
Ag	0.84	1.64	0.00	2.11	0.01
Fe	3.55	2.72	2.08	4.50	3.11
Zn	0.94	1.97	3.21	2.56	2.81
As	7.71	2.38	3.00	2.33	19.29
Sb	17.13	24.75	25.24	25.58	0.03
S	15.55	23.84	25.12	24.51	27.94

4. Discussion on the Recommended Separation Treatment

This study proposes a pilot plant flowsheet in order to extract a high-purity tetrahedrite concentrate. Experimental results indicate two distinct options for separation approaches, depending on a key parameter that proves decisive in the processing of this mineral. The determining factor is primarily whether the mineral paragenesis includes siderite, along with other associated sulphides.

Other factors, like the liberation size of tetrahedrite, are out of this assessment, as in most of the studied sites, this parameter has proven similar. It has been observed that the liberation size of tetrahedrite in all studied samples is coarse—approximately 0.5 mm—except for the sample from El Vagón Mine (Lanteira), which exhibits a slightly finer liberation size. This coarseness is advantageous for low-cost concentration processes, as it permits the use of gravity and magnetic separation techniques instead of more expensive and environmentally less sustainable flotation processes.

Thus, it is essential to initially crush the material below this liberation size, avoiding overgrinding by employing granulometric controls to minimise the generation of fines. While this may complicate the process (in the case of closed-circuit grinding), it results in a higher recovery of tetrahedrite. In an industrial setting, the circuit would consist of a primary jaw crusher, a secondary cone crusher operating in closed circuit with a vibrating screen, followed by a ball mill in closed circuit with a hydrocyclone with a cut size of approximately 1 mm. The product >0.063 mm would then be fed into a hydroclassifier, which would separate it into the following size fractions: <1 mm, 0.5 mm, 0.25 mm, 0.125 mm, and >0.063 mm. The <0.063 mm fraction would be settled and filtered for disposal; however, its concentration could be investigated. Given that this fraction constitutes a mining residue,

the objective is to pursue the most economically viable processing route, minimising re-processing costs. As such, fine concentration is more complex and would require more expensive and less sustainable techniques.

With regard to the proposed processing routes for mining residues containing tetrahedrite, it is important to distinguish between two scenarios based on the type of mineral paragenesis. The first treatment option would apply to residues originating from deposits where the mineral paragenesis includes siderite, treated here as gangue (although in the case of the sample from Torres de Albarracín, it could even be considered a potential by-product). In laboratory tests, it was necessary to deslime the samples within their respective granulometric fractions so as not to alter the behaviour of the minerals during subsequent magnetic separation. However, in the proposed pilot plant flowsheet, since ball milling is conducted under wet conditions, the <0.063 mm fraction could be eliminated directly. It would not be treated because it would require flotation or other costly methods (e.g., centrifugal gravity concentrator, discontinuous magnetic filter) for treatment.

According to the industrial design proposed in this study for such paragenesis, a hydroclassifier would be employed (following crushing and grinding) to separate the material into the same aforementioned fractions: 1–0.5 mm, 0.5–0.25 mm, 0.25–0.125 mm, and 0.125–0.063 mm. These fractions would then be dried using a rotary dryer.

Each of the dried fractions would subsequently be processed in a high-intensity magnetic separator according to the scheme illustrated in Figure 11. The diagram outlines two alternative high-intensity magnetic separation (HIMS) technologies:

- **Dry route**—using a belt-type magnetic separator with a rare-earth permanent magnet, as employed in laboratory experiments.
- **Wet route**—using a WHIMS (wet high-intensity magnetic separator), which operates with an electromagnet. While the wet route offers substantial energy savings by eliminating the need for drying the ground sample prior to magnetic separation, one must also consider the energy cost of the electromagnet, which requires an electric current to generate the magnetic field.

Multiple sorting stages are necessary to maximise the recovery of tetrahedrite, which is found in the non-magnetic fraction alongside lighter and non-magnetic minerals (e.g., quartz). The magnetic fraction primarily contains siderite, which, in some of the studied deposits, is present in such high concentrations that its recovery as a by-product could be economically justified.

For samples exhibiting a paragenesis without siderite, the proposed process begins with gravity concentration on a shaking table. As this is a wet process, no drying stage is required post-crushing and grinding (conducted in closed circuit). This type of gravity separation requires each granulometric fraction to be treated separately, thereby also demanding a preliminary classification stage using a hydroclassifier.

It is essential to control the water flow over the shaking table, along with the feed rate and table inclination, all of which must be adjusted visually according to the grain size being processed.

Subsequently, the table pre-concentrate, now reduced in volume, may undergo magnetic separation using a WHIMS unit. This eliminates the need for drying at this stage; however, since only a small amount of material is being processed, and the magnetic concentrate must ultimately be dried for potential sale, an alternative approach would be to dry the table dense product prior to magnetic separation. In this scenario, a cross-belt HIMS unit employing an electromagnet could be employed. It may also be necessary to introduce additional sorting or cleaning stages to obtain a higher-purity tetrahedrite concentrate. This flowsheet is illustrated in Figure 12.

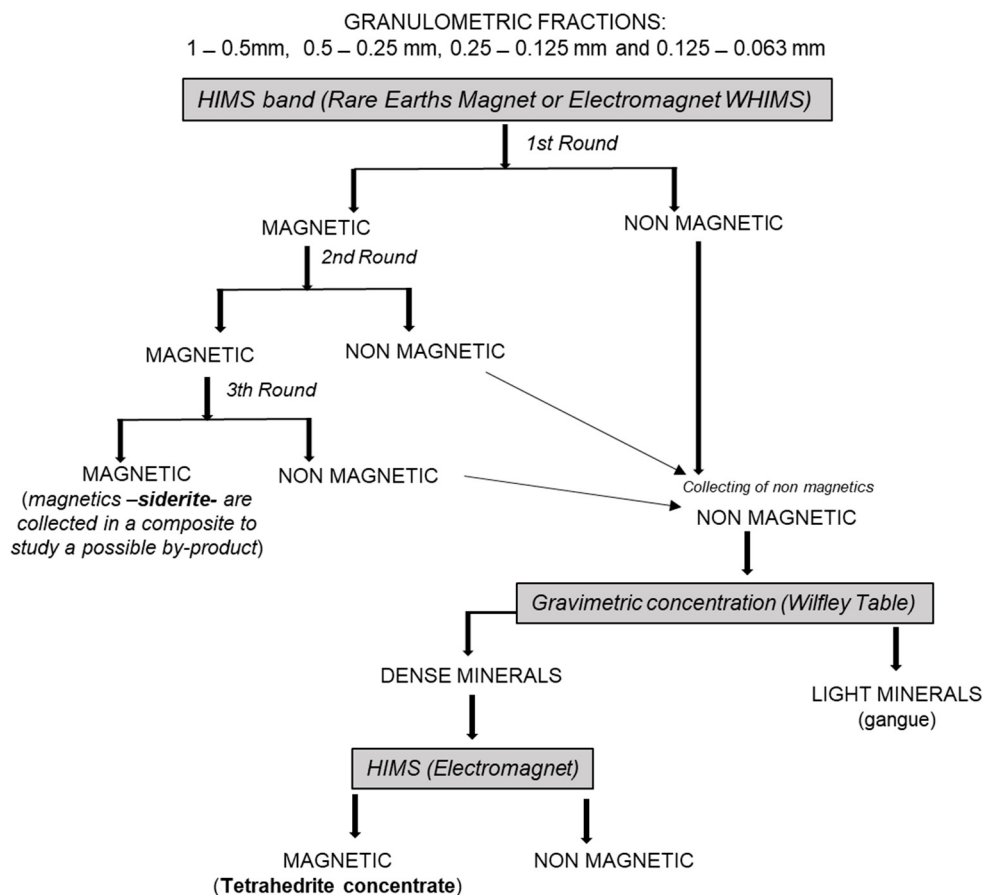


Figure 11. Treatment flowsheet proposed for the paragenesis where siderite is present.

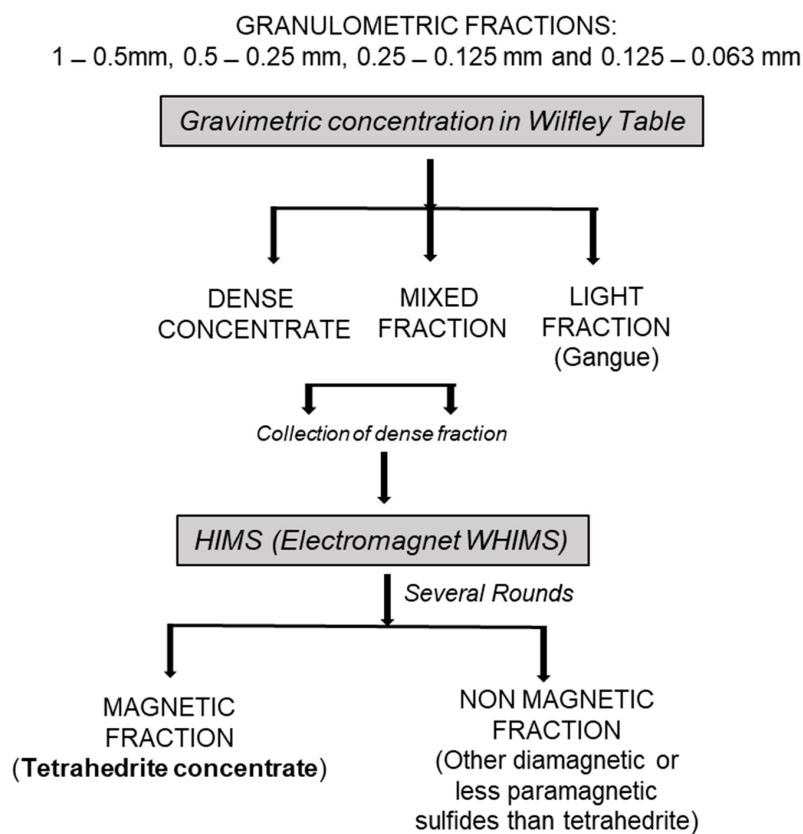


Figure 12. Treatment flowsheet proposed for the paragenesis with sulphide minerals.

In the case of La Profunda mine, the mining residue contains a certain amount of magnetite. Due to its ferrimagnetic properties, it must be removed using low-intensity magnetic separation with a ferrite permanent magnet (which can be conducted either wet or dry using a drum-type magnetic separator) before applying high-intensity magnetic separation.

5. Conclusions

This study has demonstrated the feasibility of concentrating minerals of the tetrahedrite group through simple, cost-effective physical separation techniques—specifically magnetic and gravity separation—where the liberation size of the tetrahedrite exceeds 0.063 mm.

By undertaking a prior classification of the deposits to be studied, it was possible to obtain representative samples from mineralisation types that are abundant within Spain and fulfil the aforementioned liberation size requirement.

Accordingly, the proposed methodology does not involve the use of chemical reagents, thereby eliminating the need for additional environmental impact monitoring and avoiding the generation of fine waste materials, which would otherwise be inevitable. Moreover, these physical methods are more economical and sustainable than chemical processing alternatives.

Laboratory test results revealed that the recovery rate of tetrahedrite is highly dependent on the specific characteristics of each sampled deposit. Recoveries ranged from as little as 1% in the Santísima Trinidad sample to up to 13% in the sample from La Profunda Mine. This, of course, not only reflects the difficulty in concentrating tetrahedrite in each of the samples but also indicates that the primary content of tetrahedrite in the samples was lower.

Given the distinct mineralogical characteristics of the Santísima Trinidad deposit and the effective magnetic separation of siderite, the valorisation of siderite as a by-product could be considered within this type of paragenesis. A detailed economic assessment would be necessary to determine the commercial viability of such recovery.

The final selection of the optimal technological pathway and processing flowsheet for the two studied parageneses will ultimately rely on a comprehensive techno-economic evaluation. As such, the proposed pilot plant (pre-industrial) schemes are derived exclusively from laboratory-scale analyses of the collected samples, with the principal objective being to maximise tetrahedrite recovery.

This work confirms the potential to utilise tetrahedrite minerals sourced from Spanish mining waste dumps as raw material. It must be emphasised, however, that the reported recovery data correspond specifically to the selected samples, which were intentionally chosen *in situ* to be enriched in tetrahedrite and more amenable to laboratory treatment. A full evaluation of the actual mineral grades within the waste dumps remains outstanding. Due to their intrinsically heterogeneous and variable composition, systematic drilling and geochemical analysis would be required to accurately determine the true tetrahedrite content of each site.

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