# RECOVERY OF DENSE MINERALS AS DERIVATIVE IN THE EXPLOITATION OF THE ALLUVIAL TERRACES OF THE MIÑO RIVER

# RECUPERACIÓN DE MINERALES DENSOS COMO SUBPRODUCTO EN LA EXPLOTACIÓN DE LAS TERRAZAS ALUVIALES DEL RÍO MIÑO

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**ABSTRACT**: Times the main objective of this work is to define an industrial protocol to recover dense minerals present in the alluvial quaternary terraces of the Miño River (NW Spain), rich in a fine-grained and high-density material identified as black sands. The recovery and sale of these sands implies the complete utilization of the resource; thereby the sustainability of the exploitation is enhanced and the environmental costs are reduced.

These black sands comprise two fractions of interest: a coarse-grained fraction, rich in gold, and a fine-grained fraction rich in monazite, ilmenite, zircon, garnets, rutile, andalucite and xenotime. On this second fraction, the methods to characterize the mineral grade from the chemical and mineralogical points of view were defined and the procedures to concentrate and recover these dense minerals were also established. As a result, the combination of dry techniques of separation with magnetic and electrostatic devices to treat the primary concentrate previously obtained from wet gravity concentration allowed the highest grade of the minerals of interest to be obtained.

**KEYWORDS**: Black sands, zircon, monazite, ilmenite, magnetic separator, electrostatic separator, spirals, Wilfley shaking table.

**RESUMEN:** El presente trabajo tiene como principal objetivo la concentración y refino de minerales densos presentes en las terrazas aluviales cuaternarias del río Miño (NW Spain) ricas en un material de granulometría fina y elevada densidad caracterizado como arenas negras. La recuperación de estas arenas y su salida al mercado supone el aprovechamiento completo del recurso, incidiendo en la sostenibilidad de la explotación y permitiendo reducir costes medioambientales.

Los estudios realizados en estas arenas negras revelan la existencia de dos fracciones granulométricas de interés: la más gruesa es rica en oro y la más fina en minerales densos principalmente monacita, ilmenita, circón y casiterita y en menor proporción granates, rutilo, andalucita y xenotima. Sobre esta segunda fracción se han optimizado los

métodos de caracterización química y mineralógica para determinar su ley, y los procedimientos de concentración y refinado automatizados. Como resultado, se plantea la combinación de técnicas de separación en seco con separadores magnéticos y electrostáticos para tratar el concentrado primario que se obtiene de la concentración gravitacional por vía húmeda ya existente. Los resultados obtenidos de estas pruebas indican que se pueden obtener elevadas leyes en los minerales de interés.

PALABRAS CLAVE: Arenas negras, circón, monacita, ilmenita, separador magnético, separador electrostático, espirales, mesa de sacudidas Wilfley.

## 1. INTRODUCCIÓN

In exploiting and using a natural mining resource, its properties and uses must be known in depth to plan its maximum exploitation and to satisfy industrial demands.

Full exploitation of a mining resource is of great interest, both at an economic level, since it increases its profitability and sustainability and at an environmental level, as it allows pollution of exploited area to be controlled and to reduce environmental costs. All these are interests that must be met in the exploitation, as some authors advise [1,2].

Fully exploiting a mineral resource in the case of sedimentary origin aggregates is unusual. In the terraces of the River Miño (Southern Galicia-Spain) the entire sedimentary gravel deposit is exploited, consisting of aggregates, which are rich in black sands. These have interesting concentrations of monazite, rutile, zircon and ilmenite as well as other minerals present in smaller amounts such as casiterite, garnets, staurolite, andalucite and xenotime. The existence of these black sands has led to research being considered aimed at establishing the analytical and separation methods that allow their exploitation and, therefore, achieve full exploitation of the deposit.

The main purpose of this work is, therefore, to identify analytical and separation procedures that are the most suitable for the mineralogical variability and complexity of the samples and that allow them to be profitably exploited. At a scientific level, the study of this mining resource is of great interest due to its complexity, for the large number of minerals present and their specificity, which poses a major challenge when developing not only the separation and concentration methods, but also the methodology of preparing samples and of analysis.

## 2. MATERIALS AND METHODS

The sedimentary origin deposit, where the existence has been confirmed of black sands of mining interest on which this study is focussed, belongs to the group of Quaternary Age of the Miño Valley in the area of Tui-Salvaterra, specifically at the QT3 level [3]. This level is characterised by quartzite gravels, only slightly cemented together, among which sandy passes stand out with crossed stratifications and white beds or multi-colours of clay.

The company Áridos do Mendo S.L manages these deposits and they have a treatment plant in which material coming from the quarry undergoes washing, separation, and classification processes using rotary sieves, bucket chains and screens to obtain sand (aggregate of mesh size under 4 mm) gravels (aggregates of mesh size above 4 mm) and a by- product rich in minerals of a fine mesh size and a high density that is characterised as black sands.

These black sands undergo an initial process in the plant of gravity concentration using spirals, a procedure by which particles are separated by making them slide along a circular channel through a flow film and are subject to the force of gravity, centrifugal force, the buovancy of the liquid and the friction of the channel bottom. This first phase is followed by a second gravity

concentration process on a Wilfley shaking table, similarly based on [4], in which mineral separation occurs due to the different speed of each particle depending on its size and density when it flows in a liquid that acts as a separation medium.

The samples on which this study was carried out come from the product of this first plant separation. Sampling was performed at two different points of the Wilfley table in such a way that two samples were taken: one of greater density, called sample A, and the other, of lower density called sample B.

The following analyses, also applied in [4,5], were carried out on these two samples:

- X-ray Diffraction in crystalline powder on a Siemens D5000 equipment fitted with a graphite crystal monochromator, Cu radiation $K_\alpha$, a power of 40kV and 30 mA and a flash detector. Identification of the crystalline phases was performed using the ICDD PDF2 data base.

- Scanning Electron Microscopy (SEM) using a Philips XL30 equipment, with resolution in SEM (3.5nm), back scattered electron (BSE) detector and with incorporated EDS micro-analysis. The samples were coated with carbon.

- X-ray Fluorescence analysis of pressed pellets in a Siemens SRS3000 equipment with a source with an Rh anode, a Be window (125) and a 10-60 kV and 5-100 mA X-ray generator with Spectra Plus software to evaluate the spectra. The samples were pressed at 30 tonnes with a boric acid base. For the analysis of elements, a semi-quantitative program *st-less-HS34-Vac* was used, which consists of a sweeping of spectral lines, measuring only those of maximum intensity in high sensitivity and with a mask diameter of 34 mm. The spectral lines were carefully chosen to obtain maximum signal intensity with minimum interference, as is described in [6].

Subsequently and as the particle size greatly influences the separation processes, those samples richest in the minerals of interest were sieved and the analysis of the elemental composition of each fraction was carried out by X-ray fluorescence, following the same method described previously. This sieving was performed using CONTROLS UNE 7050 series sieves of 1.25, 0.630 and 0.125 mm mesh size.

For concentrating and refining each of the minerals present in the black sands, an automated and dry separation procedure was sought that would not interfere in the normal working of the existing aggregate and sand treatment plant. This search was carried out for the size fraction richest in the minerals of interest. Two different procedures were tested for doing so, using the following equipment that is generally used for separating minerals in this type of samples:

- Electrostatic separator, which is based on the use of an electric field to separate compounds of different electrical properties, depending on their attraction or repulsion towards the field. Conductive particles are repelled by the field, whereas the non-conductive particles are attracted to it.
- Magnetic separator, based on the use of differences in magnetic susceptibility of the minerals in the presence of a magnetic field. Non-magnetic particles pass through the field unaltered, whereas magnetic particles are attracted by it.

## 3. RESULTS

From the mineralogical characterization of samples A and B, the following is deduced: sample A contains zircon as the major phase and ilmenite, casiterite, monazite, rutile, xenotime, quartz and gold as an accessory phase. Figure 1 shows the representative X-ray diffractogram of sample A. Sample B contains ilmenite as the main phase and quartz, monazite, staurolite, zircon, microcline, andalucite, rutile, anatase, ulvospinel and albite as a minor phase. Figure 2 shows a micro-photograph of sample B taken under SEM and using BSE mode which, by means of the different grey levels, allows differentiation the mineral phases present in the sample and shows the high level of variability of mineral

composition of this sample. This variability is also confirmed in sample A.

Tables 1a and 1b, show the percentages of elements expressed as oxide of the samples obtained by X-ray fluorescence. The spectral lines are shown that allowed the maximum signal intensity to be achieved with minimum interference.

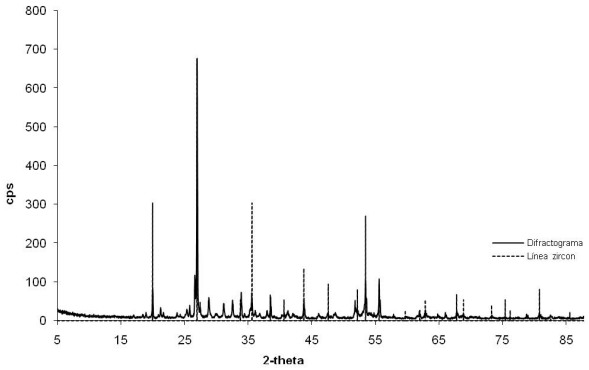


**Figure 1.** X-ray diffractogram of sample A, where it can be seen that the main phase is zircon

**Table 1a.** Concentrations of elements obtained by X-ray fluorescence of sample A, expressed as % by weight of oxides. Spectral lines selected are also indicated

| Muestra A | | |
|---|---|---|
| **Fórmula** | **Concentración (%)** | **Líneas espectrales** |
| MgO | 0,10 | Mg KA1-HS-Min |
| $Al_2O_3$ | 2,99 | Al KA1-HS-Min |
| $SiO_2$ | 11,10 | Si KA1-HS-Min |
| $P_2O_5$ | 4,53 | P KA1-HS-Min |
| $K_2O$ | 0,18 | K KA1-HS-Min |
| CaO | 0,39 | Ca KA1-HS-Min |
| $TiO_2$ | 35,61 | Ti KA1-HS-Min |
| MnO | 0,90 | Mn KA1-HS-Min |
| $Fe_2O_3$ | 16,16 | Fe KA1-HS-Min |
| ZnO | 0,09 | Zn KA1-HS-Min |
| $Y_2O_3$ | 0,65 | Y KA1-HS-Min |
| $ZrO_2$ | 18,67 | Zr KA1-HS-Min |
| $Nb_2O_5$ | 0,08 | Nb KA1-HS-Min |
| $SnO_2$ | 2,37 | Sn LA1-HS-Min |
| $La_2O_3$ | 1,23 | La LA1-HS-Min |
| $CeO_2$ | 2,12 | Ce LA1-HS-Min |
| $Pr_6O_{11}$ | 0,34 | Pr LB1-HS-Min |
| $Nd_2O_3$ | 1,29 | Nd LB1-HS-Min |
| $Sm_2O_3$ | 0,17 | Sm LB1-HS-Min |
| $Dy_2O_3$ | 0,12 | Dy LA1-HS-Min |
| $Er_2O_3$ | 0,11 | Er LB1-HS-Min |
| $Yb_2O_3$ | 0,09 | Yb LB1-HS-Min |
| $Ta_2O_5$ | 0,20 | Ta LA1-HS-Min |
| $ThO_2$ | 0,43 | Th LA1-HS-Min |
| $UO_2$ | 0,12 | U LA1-HS-Min |

**Table 1b.** Concentrations of elements obtained by X-ray fluorescence of sample B, expressed as % by weight of oxides. Spectral lines selected are also indicated

| Muestra B | | |
|---|---|---|
| **Fórmula** | **Concentración (%)** | **Línea espectral** |
| MgO | 0,69 | Mg KA1-HS-Min |
| $Al_2O_3$ | 20,40 | Al KA1-HS-Min |
| $SiO_2$ | 23,20 | Si KA1-HS-Min |
| $P_2O_5$ | 1,56 | P KA1-HS-Min |
| $K_2O$ | 0,32 | K KA1-HS-Min |
| CaO | 1,27 | Ca KA1-HS-Min |
| $TiO_2$ | 25,80 | Ti KA1-HS-Min |
| MnO | 2,23 | Mn KA1-HS-Min |
| $Fe_2O_3$ | 19,07 | Fe KA1-HS-Min |
| ZnO | 0,21 | Zn KA1-HS-Min |
| $Y_2O_3$ | 0,18 | Y KA1-HS-Min |
| $ZrO_2$ | 2,55 | Zr KA1-HS-Min |
| $SnO_2$ | 0,29 | Sn LA1-HS-Min |
| $La_2O_3$ | 0,38 | La LA1-HS-Min |
| $CeO_2$ | 0,66 | Ce LA1-HS-Min |
| $Pr_6O_{11}$ | 0,12 | Pr LB1-HS-Min |
| $Nd_2O_3$ | 0,42 | Nd LB1-HS-Min |
| $Sm_2O_3$ | 0,06 | Sm LB1-HS-Min |
| $Eu_2O_3$ | 0,32 | Eu LB1-HS-Min |
| $Gd_2O_3$ | 0,06 | Gd LA1-HS-Min |
| $Yb_2O_3$ | 0,04 | Yb LB1-HS-Min |
| $Ta_2O_5$ | 0,03 | Ta LA1-HS-Min |
| $ThO_2$ | 0,09 | Th LA1-HS-Min |
| $UO_2$ | 0,03 | U LA1-HS-Min |

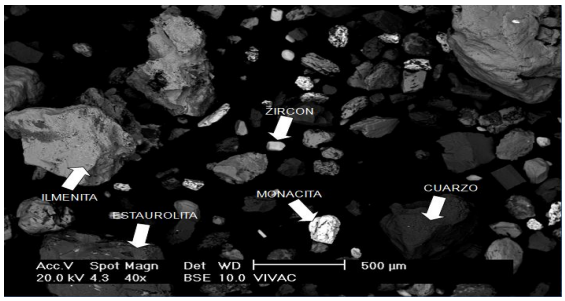


**Figure 2 .** Micro-photograph of sample B taken at SEM using BSE mode

The results obtained, on the one hand, agree with the mineral classification of the samples. Sample A has more abundant amounts of, especially, Zr, Ce, La and rare earths and, in sample B; Fe, Ti, and Al. On the other hand, it is shown that the content of dense minerals of interest is less in sample B, which was therefore discarded in the study and the subsequent analysis and separation phase will be focussed on Sample A.

Table 2 shows the size distribution of sample A and the mineralogy of each fraction

**Table 2.** Percentage by weight of the three size fractions of sample A mineral composition of each of them

| Particle size | % total weight | Main minerals |
|---|---|---|
| 1.25mm - 0.630mm | 6 | Gold, cyanite and casiterite. |
| 0.630mm - 0.125mm | 36 | Ilmenite, casiterite, rutile, Zircon, monazite and gold |
| Less than 0.125mm | 57 | Zircon, monazite, ilmenite and rutile |

Observing the results of table 2, it can be said that:

- The fraction between 1.250mm and 0.630mm is mainly rich in gold. The separation procedure for gold in this fraction, due to it complex and specific nature will be covered in a later specific study.
- The fraction between 0.630mm and 0,125mm contains both gold and dense minerals and, as gold separation will be dealt with in subsequent works, this sample will also be reserved.
- The fraction of less than 0.125mm have the greatest concentration and relative weight of minerals of interest, so separation procedures are therefore going be centred on it.

Once the sample is known that is going to be studied, consideration is given to two dry procedures with magnetic and electrostatic separators for concentrating and refining of the minerals present in the primary concentration.

Procedure 1 consists of drying the sample in an oven at 150ºC, followed by screening to select the particle size of interest, which in this specific study turned out to be that of less than 0.125 mm; this fraction is then taken to the electrostatic separator and each fraction obtained in this process is then taken to the magnetic separator.

Procedure 2 is similar to the previous in as far as drying and screening; separation is first carried out by the magnetic separator and, then, each of the fractions obtained goes through the electrostatic separator.

As a prior stage to both procedures, each of the parameters that may affect the separations in each apparatus need to be optimised, i.e., the appropriate combination of variables must be found that give the best separation, this being understood as the highest assay. Therefore, trial-error tests were carried out, verifying the results by X-ray fluorescence analysis. The values of these parameters that allowed the most ideal separation are shown in table 3. Some of them have no units as they are potentiometer positions of the equipment.
Once the equipment was optimised, the test with the procedures considered was carried out, analysing by X-ray fluorescence each of the separated fractions. The results are shown in tables 4a and 4b.

**Table 3.** Optimised parameters of the electrostatic and magnetic separators used

| Variables | Optimised parameter |
|---|---|
| **Electrostatic separator** | |
| Position of rear tray | 140mm |
| Position of front tray | 40mm |
| Position of side tray | 410mm |
| Position of thread | 40mm |
| Position of electrode | 65mm |
| Roller speed of rotation | Position 5 |
| Intensity | Position 8 |
| Feeder | position 6 |
| Voltage | 0.,4mA |
| Sample temperature | $50^{O}$ C |
| Number of passes undergone by the sample | 1 |
| **Magnetic separator** | |
| Vibration speed | Position 7 |
| Plate rotation speed | Position 6 |
| Disk height | 1 mm |
| Intensity of magnetic field | 3.5 A |
| Turning direction | Clockwise or anticlockwise |
| Sample temperature | Room temperature |
| Number of passes undergone by the sample | 1 |

**Table 4a.** Percentage by weight of the minerals of interest in the fractions obtained in process 1. nc: non-conductive, mx: mixed; c: conductive; nm: non-magnetic; M: magnetic; mm: very magnetic. Z: zircon; M: Monacite; Ilm.: Ilmenite; R: Rutile

| Elect. fraction | Magnetic fraction | Z | M | Ilm. | R |
|---|---|---|---|---|---|
| | nm | 89.1 | 3.0 | 0.8 | 2.0 |
| nc | M | 7.0 | 51.0 | 14.7 | 9.4 |
| | mm | 3.3 | 25.2 | 36.1 | 10.3 |
| | nm | 22.6 | 0.7 | 1.7 | 62.3 |
| mx | M | 22.5 | 3.6 | 57.7 | - |
| | mm | 0.6 | 1.7 | 88.0 | - |
| | nm | 7.5 | 0.5 | 2.1 | 72.3 |
| c | M | 11.9 | 1.4 | 74.5 | - |
| | mm | 0.4 | 1.1 | 88.5 | - |

**Table 4b.** Percentage by weight of the minerals of interest in the fractions obtained in process 2. nc: non-conductive, mx: mixed; c: conductive; nm: non-magnetic; M: magnetic; mm: very magnetic. Z: zircon; M: Monacite; Ilm.: Ilmenite; R: Rutile

| Magnetic fraction | Elect. Fraction | Z | M | Ilm. | R |
|---|---|---|---|---|---|
| nm | nc | 68.4 | 5.5 | 1.0 | 24.0 |
| | mx | 67.5 | 2.9 | 3.6 | 17.1 |
| | c | 60.8 | 4.7 | 1.6 | 17.9 |
| M | nc | 13.3 | 52.6 | 18.5 | 7.6 |
| | mx | 25.7 | 39.1 | 17.3 | 10.2 |
| | c | 7.2 | 49.2 | 23.1 | 10.2 |
| mm | nc | 4.0 | 25.6 | 47.2 | 15.7 |
| | mx | 2.8 | 17.1 | 49.2 | 15.3 |
| | c | 1.4 | 9.9 | 57.0 | 14.3 |

## 4. CONCLUSIONS

After chemical and mineralogical characterization of the samples from the black sands from the deposits of natural aggregates of the alluvial terraces of the River Miño and after separating and refining the fraction below 0.125mm, it can be concluded that:

The analytical techniques of X-ray Diffraction and Scanning Electron Microscopy are of great use in the mineralogical identification of the samples. However, X-ray Fluorescence is the most appropriate technique for classifying the mineral grade, not only for its rigor, but also because the treatment of samples is simple and, although initial preparation requires specialisation to choose the spectral lines and to interpret the results obtained, the technique provides a great deal of information in a short time.

The concentrating and refining procedure considered allows grades of 89% for zircon, 88% for ilmenite, 51% for monazite and 72% for rutile to be obtained. These percentages, although they may vary slightly due to the intrinsic variability in the composition of the deposit itself, indicate that the separation process developed is highly satisfactory, not only at laboratory scale, but also on an industrial scale.

The in depth knowledge of these samples and their appropriate concentration and refining method will enable subsequent trials with other samples that were mentioned previously, whose study will be carried out in a similar way to that considered here.

The results shown here, that indicate the existing of an economically interesting grade dense minerals in the deposit, are going to allow decisions to be taken about the economic sustainability of the integral exploitation of the deposit and its design in a framework of sustainable mining activity.

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