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Deliverable 3.3
Recovery of rare earths

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Table of contents

EXECUTIVE SUMMARY	11
1. INTRODUCTION	12
2. PREPARATION OF SAMPLES FOR INITIAL ANALYSIS	14
2.1. SAMPLE DRYING PROCEDURE AND HUMIDITY CALCULATION	14
2.2. SAMPLE GRAIN REDUCTION PROCEDURE	15
2.3. SAMPLE FROM THE LA MATONA DUMP (HUNOSA-SPAIN)	17
2.4. SAMPLE FROM THE EL BATÁN DUMP (HUNOSA-SPAIN)	19
2.5. SAMPLE FROM THE WĘGŁOKOKS KRAJ S.A. DUMP (POLAND)	21
2.6. SAMPLE FROM THE PREMOGOVNIK VELENJE D.O.O. DUMP (SLOVENIA)	23
3. INITIAL ANALYSIS OF THE SAMPLES	26
4. GRANULOMETRIC SEPARATION OF SAMPLES BY SIEVING	31
4.1. SIEVING OF THE LA MATONA SAMPLE (SPAIN)	32
4.2. SIEVING OF THE EL BATÁN SAMPLE (SPAIN)	34
4.3. SIEVING OF THE POLISH SAMPLE	37
4.4. SIEVING OF THE SLOVENIAN SAMPLE	38
5. ANALYSIS OF SIEVED SEPARATED SAMPLES	41
6. PULSATION BOX OR HYDRAULIC SCREEN (JIG)	49
6.1. PROCEDURE FOR THE SEPARATION OF SAMPLES BY PULSATION BOX	49
6.2. SAMPLE OF LA MATONA (SPAIN)	51
6.3. SAMPLE OF EL BATÁN (SPAIN)	51
7. ANALYSIS OF DENSITY-SEPARATED SAMPLES USING THE PULSE BOX OR HYDRAULIC SIEVE METHOD	53
8. MAGNETIC FIELD SEPARATION TEST	58
8.1. PROCEDURE FOR MAGNETIC SEPARATION OF SAMPLES	59
8.2. SAMPLE FROM LA MATONA (SPAIN)	60
8.3. SAMPLE FROM EL BATÁN (SPAIN)	61

9.	<u>ANALYSIS OF THE SAMPLES SEPARATED BY THE MAGNETIC SEPARATOR</u>	63
10.	<u>ELECTRIC FIELD SEPARATION TEST</u>	69
10.1.	PROCEDURE FOR ELECTRICAL SEPARATION OF SAMPLES	70
10.2.	SAMPLE FROM LA MATONA (SPAIN)	71
10.3.	SAMPLE FROM EL BATÁN (SPAIN)	72
11.	<u>ANALYSIS OF THE SAMPLES SEPARATED BY THE ELECTRICAL SEPARATOR</u>	73
12.	<u>SHAKING TABLE SEPARATION TEST</u>	76
12.1.	PROCEDURE FOR SHAKING TABLE SEPARATION OF THE SAMPLES	78
12.2.	SAMPLE FROM LA MATONA (SPAIN)	79
12.3.	SAMPLE FROM EL BATÁN (SPAIN)	79
13.	<u>ANALYSIS OF THE SAMPLES SEPARATED BY THE SHAKING TABLE</u>	81
14.	<u>FROTH FLOTATION TEST</u>	84
14.1.	FROTH FLOTATION PROCEDURE OF THE SAMPLES	84
14.2.	SAMPLE FROM LA MATONA (SPAIN)	86
15.	<u>ANALYSIS OF SAMPLES SEPARATED BY FROTH FLOTATION</u>	88
16.	<u>MOZLEY MULTIGRAVIMETRIC CONCENTRATION TEST (MGS)</u>	91
17.	<u>ANALYSIS OF SEPARATED SAMPLES BY MOZLEY MULTIGRAVIMETRIC SEPARATION (MGS)</u>	95
18.	<u>FEASIBILITY OF RARE EARTHS RECOVERY USING MINERALURGICAL TECHNIQUES</u>	98
	<u>CONCLUSIONS & LESSONS LEARNT</u>	100
	<u>GLOSSARY</u>	102
	<u>REFERENCES</u>	103

List of Figures

Figure 1-1. Periodic table of the elements with the rare earths labelled (IUPAC).....	12
Figure 2-1. Single acting jaw crusher and Disc mill	16
Figure 2-2. Jones or channel sampler for coarse and fine.....	16
Figure 2-3. Scales	16
Figure 2-4. Initial state of the La Matona sample	17
Figure 2-5. Grinding treatment of the La Matona sample	18
Figure 2-6. Final sample from La Matona	19
Figure 2-7. Initial state of the El Batán sample	19
Figure 2-8. Grinding treatment of the El Batán sample	21
Figure 2-9. Final sample from El Batán	21
Figure 2-10. Initial status of the Polish sample	22
Figure 2-11. Grinding treatment of the Polish sample	22
Figure 2-12. Final sample from Poland	23
Figure 2-13. Initial status of the Slovenian sample	24
Figure 2-14. Slovenian final sample	25
Figure 3-1. Graph of the quantitative analysis of rare earths	27
Figure 3-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain, Poland and Slovenia.....	28
Figure 3-3. Graph of the percentage of initial analysis of oxides of rare earths.....	30
Figure 4-1. Sieve	31
Figure 4-2. Sample of La Matona next to the siever	32
Figure 4-3. Sieve granulometric fractions, >2.0 mm (upper left), 2.0-0.5 mm (upper right), 0.5-0.1 mm (lower left), and <0.1 mm (lower right).....	33
Figure 4-4. Sectorial graph of the different fractions of the sieved La Matona sample.....	33
Figure 4-5. Samples for rare earth analysis.....	34
Figure 4-6. Sample of El Batán next to the siever	34
Figure 4-7. Sieve granulometric fractions, >2.0 mm (upper left), 2.0-0.5 mm (upper right), 0.5-0.1 mm (lower left), and <0.1 mm (lower right).....	35
Figure 4-8. Sectorial graphic of the different granulometric fractions of the sieved sample from El Batán.....	36
Figure 4-9. Samples for rare earth analysis.....	36
Figure 4-10. Particle size fractions in the sieves, >2.0 mm (left), 2.0-0.5 mm, 0.5-0.1 mm and <0.1 mm (right)	37
Figure 4-11. Sectoral chart of different fractions of sieved sample from Poland.....	37
Figure 4-12. Samples for rare earth analysis.....	38
Figure 4-13. Particle size fractions in the sieves, >2.0 mm (left), 2.0-0.5 mm, 0.5-0.1 mm and <0.1 mm (right)	39
Figure 4-14. Sector chart of different fractions of sieved sample from Slovenia	39
Figure 4-15. Samples for rare earth analysis.....	40
Figure 5-1. Graph of the quantitative analysis (ppm) of elements in the samples.....	42

Figure 5-2. Comparison of the Sc-Y element contents (ppm) of the sieved samples at all sampling points..... 43

Figure 5-3. Comparison of the ppm content of light rare earths (LREE), La, Ce, Pr and Nd in sieved samples and at all sampling points. 44

Figure 5-4. Comparative ppm content of mean rare earths (MREE), Sm, Eu and Gd of sieved samples and at all sampling points 45

Figure 5-5. Comparative ppm content of heavy rare earths (HREE), Tb, Dy, Ho, Er, Tm, Yb and Lu of sieved samples and at all sampling points. 46

Figure 5-6. Graph of the results of the percentage analysis of oxides of rare earths in samples..... 47

Figure 6-1. Pulsation box (jig) and Stove..... 49

Figure 6-2. Trays with different densities inside the stove 50

Figure 6-3. Graph of subsamples obtained in the pulse box of La Matona sample..... 51

Figure 6-4. Graph of the sub-samples obtained in the pulse box of El Batán sample. .. 52

Figure 7-1. Graph of the quantitative analysis of the samples from La Matona using the pulse box 54

Figure 7-2. Graph of the quantitative analysis of the samples from El Batán using the pulse box 54

Figure 7-3. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) using the pulse box 55

Figure 7-4. Graph of the percentage analysis of elements of the samples from La Matona obtained using the pulsation box..... 56

Figure 7-5. Graph of the percentage analysis of oxides of rare earths of the El Batán samples obtained using the pulsation box..... 57

Figure 8-1. Diagram of the operation of a magnetic drum for metal removal (Fuerstenau and Han, 2003). 59

Figure 8-2. Magnetic separator..... 60

Figure 8-3. Different fractions resulting from the magnetic separator on the La Matona sample 61

Figure 8-4. Different fractions resulting from the magnetic separator of the El Batán sample. 62

Figure 9-1. Graph of the quantitative analysis of the samples using the magnetic separator with a particle size of 0.5-2.0 mm..... 64

Figure 9-2. Graph of the percentage analysis of the 0.5-2.0 mm samples obtained by the magnetic separator..... 65

Figure 9-3. Graph of the quantitative analysis of the samples from La Matona using the magnetic separator with a particle size of 0.1-0.5 mm. 66

Figure 9-4. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the magnetic separator 66

Figure 9-5. Graph of the percentage analysis of the 0.1-0.5 mm samples obtained by the magnetic separator..... 68

Figure 10-1. Electrification by conductive induction of a conductive particle (a) and a dielectric particle (b)..... 69

Figure 10-2. Principle of operation of the phenomenon of conduction charging on mineral particles. 70

Figure 10-3. Electrical separator 71

Figure 10-4. Different fractions resulting from the electrical separator of the La Matona sample 72

Figure 10-5. Different fractions resulting from the electrical separator of the El Batán sample 72

Figure 11-1. Graph of the quantitative analysis of the samples by means of the electrical separator 74

Figure 11-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the electrical separator 74

Figure 11-3. Graph of the percentage of analysis of the samples obtained by the electrical separator 75

Figure 12-1. Particle distribution on a shaking table..... 76

Figure 12-2. Shaking table..... 78

Figure 12-3. Exit areas of the different fractions of the shaking table 78

Figure 12-4. Graph of the shaking table separation of the La Matona sample. 79

Figure 12-5. Graph of the shaking table separation of the El Batán sample by sector.. 80

Figure 13-1. Graph of quantitative analysis of the samples using shaking table..... 82

Figure 13-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the shaking table..... 82

Figure 13-3. Graph of the percentage analysis of the samples obtained using the shaking table..... 83

Figure 14-1. Separation graph in the froth flotation cell of the La Matona sample 86

Figure 14-2. Separation graph of El Batán sample in the Froth Flotation Cell..... 87

Figure 15-1. Graph of quantitative analysis of samples using froth flotation 89

Figure 15-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the froth flotation 89

Figure 15-3. Graph of percentage analysis of samples obtained by froth flotation 90

Figure 16-1. Mozley Multigravimetric Separator 92

Figure 16-2. Mozley Multigravimetric Separation (MGS) graph of La Matona sample. 93

Figure 16-3. Mozley Multigravimetric Separation (MGS) graph of El Batán sample. 94

Figure 17-1. Graph of the quantitative analysis (ppm) of the samples obtained by Mozley multigravimetric separation 96

Figure 17-2. Graph of the percentage analysis of the samples obtained by the Mozley multigravimetric separation..... 97

List of Tables

Table 1-1. Rare earth types and physical and chemical properties	13
Table 2-1. Variation in the weight of the La Matona sample and imbibition humidity .	17
Table 2-2. Calculation values of hygroscopic humidity in sample of La Matona	18
Table 2-3. Weight variation of the El Batán sample and imbibition humidity	20
Table 2-4. Calculation values of hygroscopic humidity in a sample from El Batán	20
Table 2-5. Weight variation of the Polish sample	22
Table 2-6. Variation of Slovenian sample weight and imbibition humidity	24
Table 2-7. Calculation values for hygroscopic humidity in Slovenian samples	25
Table 3-1. Chosen analysis methods	26
Table 3-2. Results of quantitative analysis (ppm) of elements.....	27
Table 3-3. Results of the percentage analysis of oxide compounds.....	29
Table 4-1. Granulometric fractions of the La Matona sample.....	32
Table 4-2. Granulometric fractions of the El Batán sample.....	35
Table 4-3. Particle size fractions of the Polish sample	37
Table 4-4. Grain size fractions of the Slovenian sample.....	38
Table 5-1. Results of quantitative analysis (ppm) of elements in sieved samples.....	41
Table 5-2. Results of the percentage analysis of oxides of rare earths in the sieved samples.....	47
Table 6-1. Densitometrically distinct sub-samples of the La Matona sample	51
Table 6-2. Desymmetrically distinct sub-samples of the El Batán sample.....	52
Table 7-1. Results of the quantitative analysis (ppm) of elements in the samples from the pulsation box.	53
Table 7-2. Results of the percentage analysis (%) of elements in the samples of the pulsation box	56
Table 8-1. Magnetic intensity required (Teslas) in the separation of different magnetic minerals	58
Table 8-2. Magnetic separation of the La Matona sample.....	61
Table 8-3. Magnetic separation of the El Batán sample.....	62
Table 9-1. Results of the quantitative analysis (ppm) of elements of the samples obtained by the magnetic separator with a particle size of 0.5-2.0 mm.	63
Table 9-2. Results of the percentage analysis (%) of the samples from the magnetic separator	64
Table 9-3. Results of the quantitative analysis (ppm) of elements of the samples obtained by the magnetic separator with a particle size of 0.1-0.5 mm.	65
Table 9-4. Results of the percentage analysis of the samples obtained using the magnetic separator with a particle size of 0.1-0.5 mm.....	67
Table 10-1. Electrical separation of La Matona sample	71
Table 10-2. Electrical separation of the El Batán sample	72
Table 11-1. Results of the quantitative analysis (ppm) of elements in the samples obtained by the electrical separator.	73

Table 11-2. Results of the percentage analysis (%) of the samples from the electrical separator 75

Table 12-1. Gravimetric shaking table separation of the La Matona sample 79

Table 12-2. Gravimetric shaking table separation of the El Batán sample 80

Table 13-1. Results of the quantitative analysis (ppm) of elements of the samples obtained by the shaking table..... 81

Table 13-2. Results of the percentage analysis (%) of the shaking table samples..... 83

Table 14-1. Foam Flotation Cell Separation of the La Matona Sample 86

Table 14-2. Foam Flotation Cell Separation of El Batán Sample 86

Table 15-1. Results of the quantitative analysis (ppm) of elements in the samples obtained by froth flotation 88

Table 15-2. Results of percentage analysis (%) of froth flotation samples..... 90

Table 16-1. Results of the Mozley Multigravimetric Separation (MGS) of La Matona sample. 93

Table 16-2. Results of Mozley Multigravimetric Separation (MGS) of El Batán sample. 94

Table 17-1. Results of the quantitative analysis (ppm) of elements in the samples obtained by the Mozley multigravimetric separation. 95

Table 17-2. Results of the percentage analysis (%) of the samples from the Mozley multigravimetric separation..... 96

Executive Summary

In this Deliverable we will try to identify potential approaches for the concentration of mixed rare earth oxides from fine coal waste from the three case studies: Spain (HUNOSA), Poland (WEGLO), and Slovenia (PVM).

The samples will first be divided into different particle size fractions >2.0 mm, 2.0/0.5 mm, 0.5/0.1 mm, <0.1 mm, because these are the sizes that would be obtained at various process points in the coal washing plant. Subsequently, laboratory analysis will be developed for each fraction to identify rare earth contents and the mineralogical species present. The methods will be, e.g., Inductively Coupled Plasma-Atomic Emission Spectrometers (ICP-AES) and X-Ray Fluorescence (XRF).

With the data obtained, rare earth release and concentration analyses will be carried out to decide the particle sizes that will allow a higher recovery of rare earths.

Next, since almost all rare earth minerals are very dense, gravimetric concentration analysis will be developed in the first place to obtain a dense wet concentrate. The equipment to be used will depend on the liberation analysis: multigravity separator for sizes <0.1 mm, shaking tables for sizes between 0.1 and 0.5 mm, and pulsation box for sizes between 0.5 and 2.0 mm.

Secondly, based on the paramagnetic character of rare earth minerals, the dense concentrate will be subjected to high field strength magnetic separation, using a dry route for particle sizes >0.1 mm.

Next, based on the non-conductive character of most rare earth minerals, a high voltage electric field separation (30-40 kV) will be carried out for particle sizes between 0.1 and 0.5 mm (dry route).

Finally, a froth flotation test for particles >0.02 mm will also be carried out.

1. Introduction

This work package's main objective is to analyse the deployment of circular economy technologies for the three case studies based on the valorisation of fine coal waste. Specific objectives are:

1. Assess the development of high-density fluids required for the unconventional pumped hydro.
2. Evaluate the development of soil substitutes to restore waste heaps using different combinations of fine coal waste with other industrial/organic waste.
3. Identify potential approaches for the concentration of mixed rare earth oxides.
4. Analyse the technical specifications, cost data and operational constraints of the selected alternatives for each circular economy technology.
5. Prepare a detailed assessment of the job creation potential of each alternative in terms of production capacity, both for commissioning and operation.

This task was led by UNIOVI and developed at the Mineral Processing Laboratory of the School of Mining, Energy and Materials Engineering, with fine coal waste from the three case studies: Węłłokoks Kraj S.A. (WEGLO), Hulleras del Norte S.A. S.M.E. (HUNOSA) and Premogov-nik Velenje d.o.o. (PVM) will supply the fine coal waste to identify potential approaches at TRL 5-6 for the concentration of rare earths.

The International Union of Applied and Pure Chemistry (IUPAC) defined rare earths as a group of metallic chemical elements of the periodic table known as Lanthanides plus Scandium and Yttrium (Figure 1-1).

The figure shows a standard periodic table with a legend and a red box highlighting the rare earth elements. The legend includes categories like 'metales alcalinos', 'metaloideos', 'alcalinotérreos', 'no metales', 'otros metales', 'halógenos', 'metales de transición', 'gases nobles', 'lantánidos', 'actínidos', 'elementos desconocidos', and 'metales de transición especiales'. The red box highlights the following elements: Scandium (Sc), Yttrium (Y), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu).

Figure 1-1. Periodic table of the elements with the rare earths labelled (IUPAC)

These elements can be divided into three groups: light (LREE), medium (MREE) and heavy (HREE) as shown in Table 1-1.

Table 1-1. Rare earth types and physical and chemical properties

Element	Symbol	Type	Atomic n ^o	Atomic Weight	Density (g/cm ³)	Melting point °C	Boiling point (°C)	Vickers Hardness	Crystal Structure
Scandium	Sc	-	21	44.95	2.989	1541	2832	85	Hexagonal
Yttrium	Y	-	39	88.90	4.469	1522	3337	38	Hexagonal
Lanthanum	La	Light rare earths (LREE)	57	138.90	6.146	918	3469	37	Hexagonal
Cerium	Ce		58	140.11	8.160	789	3257	24	Cubic
Praseodymium	Pr		59	140.90	6.773	931	3127	37	Hexagonal
Neodymium	Nd		60	144.24	7.008	1021	3127	35	Hexagonal
Promised	Pm		61	145.00	7.264	1042	3000	-	Hexagonal
Samarium	Sm		Middle rare earths (MREE)	62	150.36	7.520	1074	1900	45
Europium	Eu	63		151.96	5.244	822	1597	17	Cubic
Gadolinium	Gd	64		157.25	7.901	1313	3233	57	Hexagonal
Terbium	Tb	Heavy rare earths (HREE)	65	158.92	8.230	1356	3041	46	Hexagonal
Dysprosium	Dy		66	162.50	8.551	1412	2562	42	Hexagonal
Holmium	Ho		67	164.93	8.795	1474	2720	42	Hexagonal
Erbium	Er		68	167.26	9.066	1529	2510	44	Hexagonal
Thulium	Tm		69	168.93	9.321	1545	1727	48	Hexagonal
Ytterbium	Yb		70	173.04	6.966	819	1466	21	Cubic
Lutetium	Lu		71	174.97	9.841	1663	3315	77	Hexagonal

2. Preparation of samples for initial analysis

This section will describe the procedure used to prepare samples for initial analysis in an accredited laboratory.

It is necessary to point out that in the case of HUNOSA some all-one samples have been taken since the El Batán coal preparation plant only carries out a pre-treatment by screening the material from the San Nicolás well, which is the company's only active mine.

To have a comparison, two samples have been taken, one from the El Batán coal preparation plant and another from the old coal preparation plant tailings that were accumulated in the La Matona dump. Five bags of between 20 and 25 kg of material were taken from the El Batán coal preparation plant and as many from the La Matona dump.

2.1. Sample drying procedure and humidity calculation

The procedure, using the UNE 32-001-81 Standard, for drying the sample, at laboratory temperature, and calculating the **imbibition humidity (X)** was as follows:

- Place the material from a sample bag in an appropriate number of large trays, with a volume between 0.015m³ (0.50m x 0.30m x 0.10m) and 0.013m³ (0.51m x 0.34m x 0.075m), so that it dries in a time of approximately one or two weeks. Between 5 and 10 kg of sample will be placed per tray.
- The quantity of between 1 and 3 kg of sample is taken in a smaller tray, with a volume of 0.004m³ (0.30m x 0.24m x 0.055m), for the determination of imbibition humidity.
 - The empty tray is weighed (P₁) and its value is recorded.
 - The tray with the sample is weighed again (P₂).
 - The weight of the empty tray is subtracted, and the weight of the sample (P₃) is obtained.

$$P_3 = P_2 - P_1$$

- It is left to dry at laboratory temperature until the weight stabilizes, checking every 3 days the variation in weight in grams and calculating the percentage of humidity lost. This process can take approximately 1-2 weeks.
- Once the weight stabilizes, the imbibition humidity is obtained.

The procedure, using the UNE 32-001-81 Standard, for drying the sample, in a laboratory drying oven, and calculating the **hygroscopic humidity (M)** was as follows:

- An empty tray is weighed and its value is noted (m_2).
- The empty tray is placed in the oven at a temperature between 378 and 383 K (105 and 110°C) and its air atmosphere is renewed 3 to 5 times per hour and it is weighed again when hot, noting its new value (m_4).
- The sample from the imbibition humidity is placed in the tray, distributing it evenly over the entire surface (maximum 1 g/cm²), the tray plus the sample (m_1) is weighed and placed in the oven to dry.
- It is kept at that temperature until constant mass. The drying time ranges between 3 and 6 hours.
- Once the weight of the tray plus the hot sample has stabilized, it is taken to the balance and its value (m_3) is recorded.
- The hygroscopic humidity of the analyzed sample is obtained by means of the following expression:

$$M = \frac{(m_1 - m_4) - (m_3 - m_2)}{(m_1 - m_4)}$$

m_1 = mass, in grams, of tray and sample as received

m_2 = mass, in grams, of the empty tray

m_3 = mass, in grams, of tray and sample after heating

m_4 = mass, in grams, of empty, dry tray

When the sample, as in this case, has been air-dried, the **total humidity (H_T)**, in percentage, is calculated using the following formula:

$$H_T = X + M (1 - (X / 100))$$

X = Imbibition humidity in percent

M = Hygroscopic humidity in percent

2.2. Sample grain reduction procedure

Next, once dry, the procedure that has been used to reduce the grain of the samples in order to obtain an optimal size for the analysis of rare earths in the laboratory will be described.

The machines used are the following:

- Single acting jaw crusher (Figure 2-1, left).
- Disc mill (Figure 2-1, right)

- Jones or channel sampler (Figure 2-2).
- Scales (Figure 2-3).



Figure 2-1. Single acting jaw crusher and Disc mill

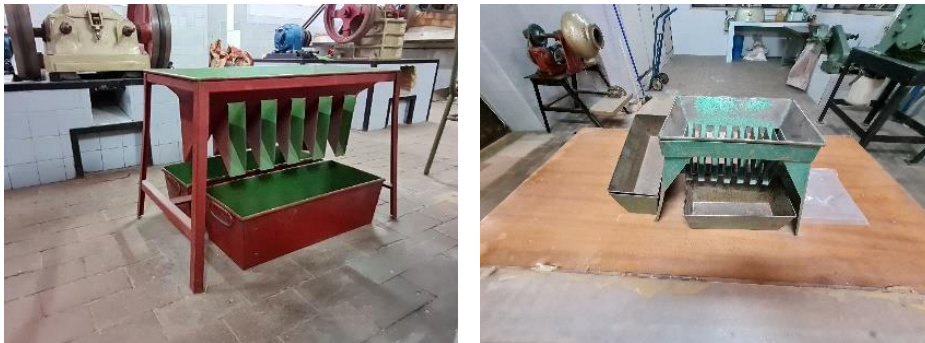


Figure 2-2. Jones or channel sampler for coarse and fine



Figure 2-3. Scales

Initially, the machines to be used must be cleaned in order to eliminate any impurities that may exist from previous procedures that could contaminate the samples. Initially, the sample is passed through the jaw crusher, which crushes it, giving it a maximum size of 2 cm, optimal for introducing it into the disc mill, which reduces it to a maximum size of 5 mm. Once this size has been achieved, the desamplers will be used to obtain the appropriate amount of sample for analysis.

2.3. Sample from the La Matona dump (HUNOSA-Spain)

Next, the drying procedure of the sample extracted from the La Matona of HUNOSA dump will be described. The initial state of the La Matona sample is shown in Figure 2-4.



Figure 2-4. Initial state of the La Matona sample

Initially, one of the bags, of approximately 20 kg of sample was placed in two large trays with a volume of 0.015m³ each and the amount of 2526.60 g in another small tray, 0.004m³, which weighs 551.50 g when empty. After 4 days, the small tray was weighed again, after 8 days it was weighed again, verifying that the weight had not yet stabilized, and after 12 days, the same operation was carried out, observing the final stabilized weight and being able to obtain the imbibition humidity of the 12.6%. The results obtained are those presented in the following table (Table 2-1):

Table 2-1. Variation in the weight of the La Matona sample and imbibition humidity

DATE	WEIGHT (g)		VARIATION	
	Sample+tray	Sample	g	%
28/02/2022	3075.10	2523.60	0.00	0.00%
04/03/2022	2830.40	2278.90	-244.70	-10.70%
07/03/2022	2792.10	2240.60	-38.30	-1.70%
09/03/2022	2787.70	2236.20	-4.40	-0.20%
11/03/2022	2787.70	2236.20	0.00	0.00%
TOTAL VARIATION:			-287.40	-12.6%

Before placing the sample in the tray for humidity calculation, it was placed in the oven at a temperature between 378 and 383 K (105 and 110°C), and said tray was weighed once dry, obtaining a value of 550.7g This value is obtained to proceed to the calculation of the hygroscopic humidity, which once the formula was applied turned out to be 0.9%. The values used for the calculation are detailed in Table 2-2.

Table 2-2. Calculation values of hygroscopic humidity in sample of La Matona

CONCEPT	SYMBOL	MASS (g)
Initial mass in grams of tray + sample	m_1	2787.7
Mass in grams of initial empty tray	m_2	551.5
Mass in grams of tray + sample after heating	m_3	2768.3
Mass in grams of empty and dry tray	m_4	550.7

Once the imbibition and hygroscopic humidity are obtained, the **total humidity** is obtained, which turned out to be 13.4%.

Next, once the sample was dry, it was passed through the jaw crusher, obtaining the optimum size for the disc mill. Figure 2-5 shows the different machines through which the La Matona sample was passed, as well as the grain size obtained in the jaw crusher.



Figure 2-5. Grinding treatment of the La Matona sample

After grinding the material, it is passed through the large desampler and then through the finer one to obtain a sample bag for analysis of 982.10g (Figure 2-6). From this sample, the amount required by the laboratory to carry out the rare earth analyses will be extracted, passing it again through the fine sampler.



Figure 2-6. Final sample from La Matona

2.4. Sample from the El Batán dump (HUNOSA-Spain)

Next, the drying procedure of the sample extracted from the El Batán coal preparation plant of HUNOSA will be described. The initial state of the El Batán sample is shown in Figure 2-7.



Figure 2-7. Initial state of the El Batán sample

Initially, one of the bags, of approximately 25 kg, of sample was placed in four large trays with a volume of 0.013m³ each and the amount of 1357.80g in another small tray, 0.004m³, which weighs 565.50g when empty. After 4 days the small tray was weighed again, after 8 days it was weighed again, verifying that the weight had already stabilized and being able to obtain imbibition humidity of 6.16%. The results obtained are those presented in the following table (Table 2-3):

Table 2-3. Weight variation of the El Batán sample and imbibition humidity

DATE	WEIGHT (g)		VARIATION	
	Sample+Tray	Sample	g	%
28/02/2022	1923.30	1357.80	0.00	0.00%
04/03/2022	1845.20	1279.70	-78.10	-6.10%
07/03/2022	1844.50	1279.00	-0.70	-0.05%
09/03/2022	1844.70	1279.20	0,.0	0.02%
11/03/2022	1844.50	1279.00	-0.20	-0.02%
TOTAL VARIATION:			-78.80	-6.16%

Before placing the sample in the tray for humidity calculation, it was placed in the oven at a temperature between 378 and 383 K (105 and 110°C), and said tray was weighed once dry, obtaining a value of 564.7g This value is obtained to proceed to the calculation of the hygroscopic humidity, which once the formula was applied turned out to be 0.6%. The values used for the calculation are detailed in Table 2-4.

Table 2-4. Calculation values of hygroscopic humidity in a sample from El Batán

CONCEPT	SYMBOL	MASS (g)
Initial mass in grams of tray + sample	m ₁	1844.5
Mass in grams of initial empty tray	m ₂	565.5
Mass in grams of tray + sample after heating	m ₃	1840.7
Mass in grams of empty and dry tray	m ₄	564.2

Once the imbibition and hygroscopic humidity have been obtained, the **total humidity** is obtained, which turned out to be 6.6%.

Next, once the sample was dry, it was passed through the jaw crusher, obtaining the optimum size for the disc mill. In the Figure 2-8, you can see the difference in the grain size of the sample passed through the jaw crusher and after passing it through the disc mill.



Figure 2-8. Grinding treatment of the El Batán sample

After grinding the material, it is passed through the large sampler and then through the finer one to obtain a sample bag for analysis of 519.30g (Figure 2-9). From this sample, the amount required by the laboratory to carry out the rare earth analyzes will be extracted, passing it again through the fine sampler.



Figure 2-9. Final sample from El Batán

2.5. Sample from the Węglokoks Kraj S.A. dump (Poland)

The drying procedure of the hard coal sample extracted from Węglokoks Kraj S.A. (WEGLO) will be described below.

Initially, one of the bags of approximately 15 kg of sample was placed in two large trays with a volume of 0.013 m³ each and the amount of 1357.80 g in another small tray, 0.004 m³, which weighs 565.50 g empty as shown in Figure 2-10.

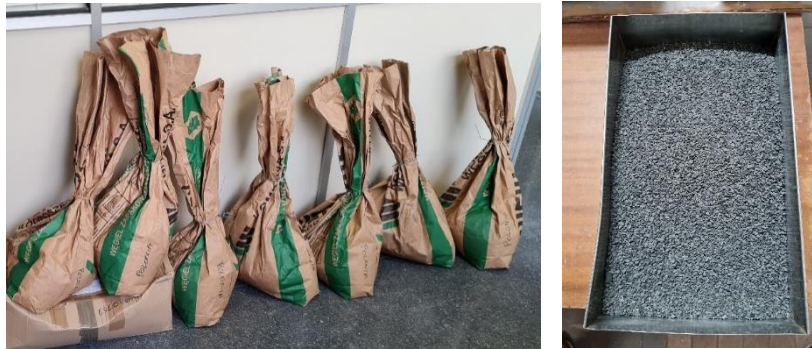


Figure 2-10. Initial status of the Polish sample

After 3 days, the small tray was weighed again and no variation in weight was observed, so it was not possible to calculate the humidity because the sample arrived completely dry. The results obtained are presented in Table 2-5.

Table 2-5. Weight variation of the Polish sample

DATE	WEIGHT (g)		VARIATION	
	Sample+tray	Sample	g	%
21/02/2023	1540.00	978.50	0.00	0.00%
24/02/2023	1540.00	978.50	0.00	0.00%
	TOTAL VARIATION:		0.00	0.00%

The sample was then passed through the disc mill (Figure 2-11) resulting in a 975.30 g bag ready for further analysis and testing.



Figure 2-11. Grinding treatment of the Polish sample

After grinding, the material is passed through the large desampler and then through the finer desampler to obtain a 50 g sample bag for analysis (Figure 2-12).



Figure 2-12. Final sample from Poland

2.6. Sample from the Premogovnik Velenje d.o.o. dump (Slovenia)

The description of the Slovenian sample is as follows:

- The sample is a combination of wastes mixed in Slovenia's coal power plant (Termoelektrarna Šoštanj - TEŠ), called Stabilizat and has ratio:
 - fly ash : gypsum : slug : muds = 45-75 : 10-55 : 0-20 : 0-2
 - And water.
- Stabilizat is product where gypsum is stabilized with fly ash. Slug and mud represent small aggregate. Fresh product must contain at least 45% of fly ash and not more than 55% gypsum regarding dry mass.

Detailed description (see Commission notice on technical guidance on the classification of waste CELEX_52018XC0409(01)_EN_TXT.pdf):

- 10 01 01 bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10 01 04) ANH
- 10 01 02 coal fly ash ANH
- 10 01 05 calcium-based reaction wastes from flue-gas desulphurisation in solid form ANH
- 10 01 07 calcium-based reaction wastes from flue-gas desulphurisation in sludge form ANH
- 19 09 03 sludges from decarbonation ANH
- 19 09 06 solutions and sludges from regeneration of ion exchangers ANH

Muds from closed water circuits and are mixture of upper listed wastes.

The drying procedure of the sample from Premogovnik Velenje d.o.o. will be described below.

Initially, one of the received boxes of approximately 20 kg of sample was placed in three large trays with a volume of 0.013 m³ each and the amount of 518.30 g was placed in another small tray, 0.004 m³, which weighs 567.10 g empty as shown on the Figure 2-13.



Figure 2-13. Initial status of the Slovenian sample

After 3 days the small tray was weighed again, after 4 days it was weighed again without stabilising the weight and finally after 14 days it was found that the weight had stopped varying and the imbibition humidity of 10.51% was obtained. The results obtained are as shown in the Table 2-6.

Table 2-6. Variation of Slovenian sample weight and imbibition humidity

FECHA	WEIGHT (g)		VARIATION	
	Sample+Tray	Sample	g	%
21/02/2023	1085.40	518.30	0.00	0.00%
24/02/2023	1031.80	464.70	-53.60	-10.34%
28/02/2023	1031.00	463.90	-0.80	-0.17%
14/03/2023	1031.00	463.90	0,00	0.00%
TOTAL VARIATION:			-78.80	-10.51%

Before placing the sample in the tray to calculate the moisture content, it was placed in the oven at a temperature between 378 and 383 K (105 and 110oC), and the tray was weighed once it was dry, obtaining a value of 561.8 g. This value was obtained in order to calculate the hygroscopic humidity, which, once the formula was applied, was 1.8%. The values used for the calculation are detailed in the Table 2-7.

Table 2-7. Calculation values for hygroscopic humidity in Slovenian samples

CONCEPT	SYMBOL	MASS (g)
Initial mass in grams of tray + sample	m_1	1135.8
Mass in grams of initial empty tray	m_2	563.2
Mass in grams of tray + sample after heating	m_3	1126.9
Mass in grams of empty and dry tray	m_4	561.8

Once the imbibition and hygroscopic moisture content was obtained, the **total humidity** content was 12.12%.

Then, once the sample was dry, it was passed through the disc mill, through the large sampler and then through the finer sampler to obtain a 50 g sample bag for analysis (Figure 2-14). From this sample, the quantity required by the laboratory for rare earth analysis is extracted by passing it through the fine desampler again.



Figure 2-14. Slovenian final sample

3. Initial analysis of the samples

This section presents the result of the initial analysis of the samples carried out in an accredited laboratory: ALS Laboratory Group, S.L. (www.alsglobal.com/geochemistry).

A quantitative analysis of some elements (ppm) called ME-MS89L and another percentage analysis of other elements and their oxides (%) called ME_XRF30 had been requested, as shown in Table 3-1. Chosen analysis methods, from the documentation provided by the laboratory. In addition, by means of the ME-MS89L method, the elements Hf and Zr that were not reflected in the laboratory tables were introduced for analysis. Prior to analysis, the samples were pulverized to a size of 75 µm. Sample drying procedure and humidity calculation.

Table 3-1. Chosen analysis methods

CODE		ANALYTES & RANGES (ppm)							
ME-MS89L™ 0.2g sample	Ag	5-12,500	Eu	0.03-25,000	Nb	0.8-25,000	Te	0.5-25,000	
	As	4-25,000	Fe	0.05%-25%	Nd	0.07-25,000	Th	0.1-25,000	
	B*	8-25,000	Ga	0.5-25,000	Ni	10-25,000	Ti	0.005%-25%	
	Ba	2-25,000	Gd	0.03-25,000	Pb	0.5-25,000	Tl	0.02-25,000	
	Be	0.4-25,000	Ge	0.5-25,000	Pr	0.03-25,000	Tm	0.01-25,000	
	Bi	0.1-25,000	Ho	0.01-25,000	Rb	0.5-25,000	U	0.2-25,000	
	*B-MS89L	Ca	0.1%-25%	In	0.3-25,000	Re	0.01-25,000	V	1-25,000
		Cd	0.8-25,000	K	0.05%-25%	Sb	0.3-25,000	W	0.3-25,000
		Ce	0.2-25,000	La	0.08-25,000	Se	3-25,000	Y	0.2-25,000
		Co	0.5-25,000	Li	2-25,000	Sm	0.04-25,000	Yb	0.02-25,000
		Cs	0.1-25,000	Lu	0.05-25,000	Sr	3-25,000	Zn	10-25,000
		Cu	20-25,000	Mg	0.01%-30%		20-25,000		
		Dy	0.03-25,000	Mn	10-25,000	Ta	0.04-25,000		
	Er	0.02-25,000	Mo	2-25,000	Tb	0.01-25,000			

*B-MS89L - Glassless digestion and analysis to eliminate boron from labware

CODE		ANALYTES & RANGES (%)				
ME_XRF30 0.7g sample	CeO ₂	0.01-50	Ho ₂ O ₃	0.01-10	Sm ₂ O ₃	0.01-10
	Dy ₂ O ₃	0.01-10	La ₂ O ₃	0.01-50	Tb ₄ O ₇	0.01-10
	Er ₂ O ₃	0.01-10	Lu ₂ O ₃	0.01-10	Tm ₂ O ₃	0.01-10
	Eu ₂ O ₃	0.01-10	Nd ₂ O ₃	0.01-10	Y	0.01-10
	Gd ₂ O ₃	0.01-10	Pr ₆ O ₁₁	0.01-10	Yb ₂ O ₃	0.01-10

The results of the quantitative analyses of the initial crude sample, in parts per million (ppm), obtained are shown in Table 3-2, as well as in the graph in Figure 3-1. The values corresponding to the sample from the La Matona dump are shown in blue, those related to the sample from the El Batán washery in orange, those related to the sample from Poland in green and those related to the sample from Slovenia in purple.

Table 3-2. Results of quantitative analysis (ppm) of elements

TYPE	ELEMENT	ANALYSIS (ppm)			
		LA MATONA SPAIN	EL BATÁN SPAIN	POLAND	SLOVENIA
-	Sc	20.20	5.90	20.00	20.00
-	Y	24.20	19.40	29.80	32.00
LREE	La	4.68	3.85	28.80	32.90
	Ce	71.20	66.90	60.50	64.80
	Pr	7.88	7.64	7.51	7.99
	Nd	30.20	27.30	28.00	31.90
MREE	Sm	5.78	5.33	6.38	6.21
	Eu	23.30	23.20	1.66	2.02
	Gd	1.30	1.20	5.25	5.76
HREE	Tb	0.87	0.68	0.94	1.07
	Dy	2.69	2.07	5.68	6.27
	Ho	0.29	0.29	0.96	1.10
	Er	1.21	1.03	3.44	3.04
	Tm	0.41	0.28	0.46	0.41
	Yb	2.52	2.13	2.86	2.94
	Lu	0.31	0.20	0.39	0.32
TOTAL		197.04	167.40	202.63	218.73

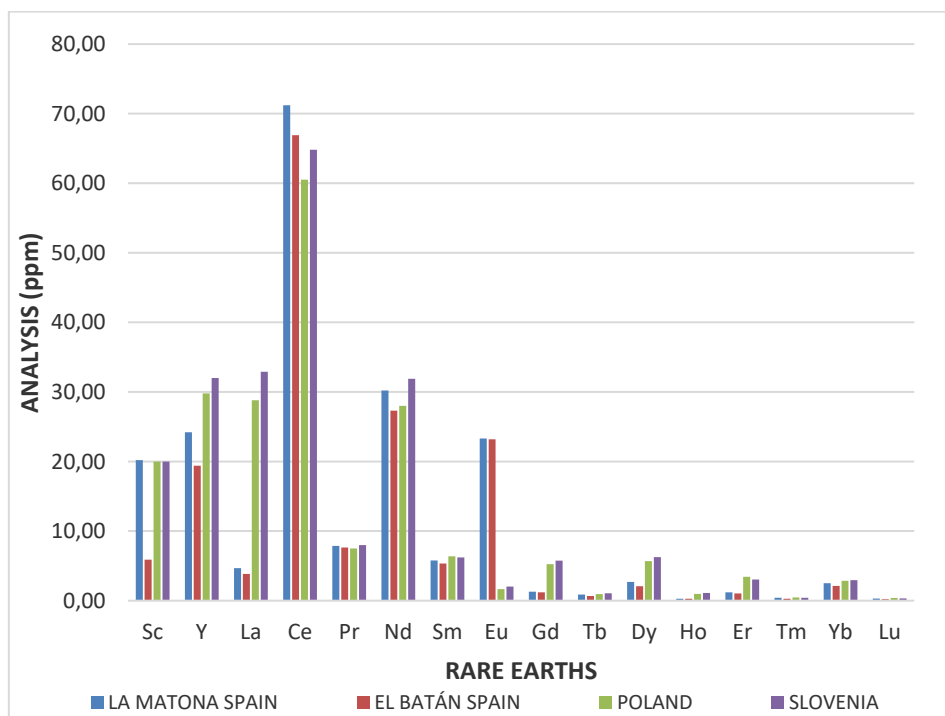


Figure 3-1. Graph of the quantitative analysis of rare earths

In the upper left graph of Figure 3-2 it can be seen that the Sc content is equal to 20 ppm in all sampling points except in El Batán which is reduced to 5.90 ppm. Y has a higher variability ranging from 19.40 ppm in El Batán to 32 ppm in Slovenia.

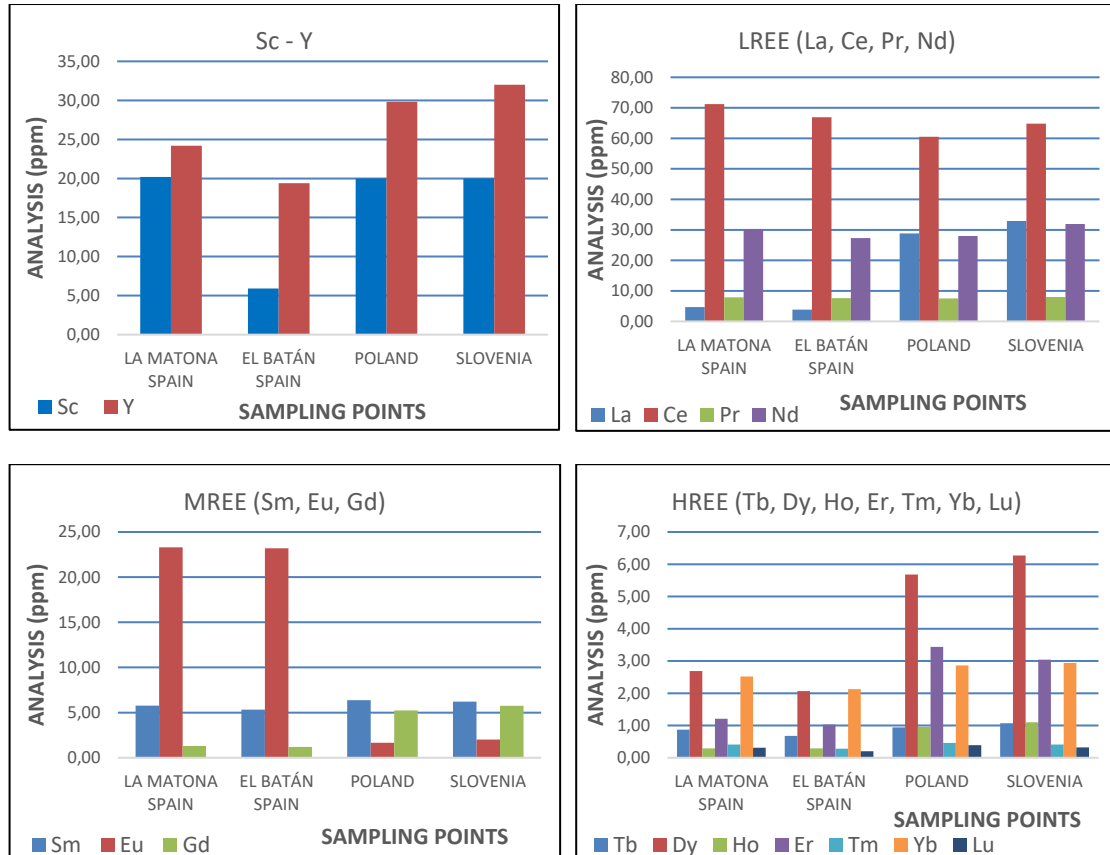


Figure 3-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain, Poland and Slovenia

The top right graph shows the LREE results. It can be seen that the Spanish samples have much lower Lanthanum (La) content (3.85 - 4.68 ppm) than the Polish (28.8 ppm) and Slovenian (32.90 ppm) samples. Cerium (Ce) content is much more abundant than the rest of the elements of this group in all the samples, ranging between 60.50 and 71.20 ppm. The samples have a low Praseodymium (Pr) content ranging from 7.51 to 7.99 ppm. Neodymium (Nd) has a similar concentration in all samples ranging between 27.30 and 31.90 ppm.

The bottom left graph shows the results of the MREE analysis. The concentration of Samarium (Sm) is similar in all sampling points ranging from 5.33 to 6.38 ppm. The Europium (Eu) content is much more abundant in the Spanish samples at around 23.3 ppm compared to the Polish (1.66 ppm) and Slovenian (2.02 ppm) samples. Gadolinium (Gd) is more abundant in the Polish (5.25 ppm) and Slovenian (5.76 ppm) samples than in the Spanish (1.30 ppm) samples.

The lower right graph shows the results of the HREE analysis. The concentration of Terbium (Tb) is similar in all sampling points, ranging from 0.68 to 1.07 ppm. The Dysprosium (Dy) content is much higher in the Polish (5.68 ppm) and Slovenian (6.27 ppm) samples compared to the Spanish samples (2.07 - 2.69 ppm). The concentration of Holmium (Ho) is slightly higher in the Polish and Slovenian samples (0.96 - 1.10 ppm) than in the Spanish samples (0.29 ppm). Erbium (Er) has a higher concentration in Poland (3.44 ppm) and Slovenia (3.04 ppm) than in Spain (1.03-1.21 ppm). The other elements show similar concentrations in all sampling points, with Thulium (Tm) ranging between 0.28 and 0.46 ppm, Ytterbium (Yb) between 2.13 and 2.94 ppm and Lutetium (Lu) between 0.20 and 0.39 ppm.

The results of the percentage analysis obtained are shown in Table 3-3, as well as in the graph in Figure 3-3. It should be noted that the percentage of the oxides of the elements in the Spanish samples are below the detection limit of 0.01%, while in the Polish and Slovenian samples they are slightly higher. Only those elements or compounds that could be detected are represented in the graph. It can be observed that most of the analysed compounds are below the detection limit. A slight increase in the concentrations of CeO₂, Nd₂O₃, Tb₄O₇ can be observed in the Slovenian samples with respect to the rest of the sampling points without being significant.

Table 3-3. Results of the percentage analysis of oxide compounds

TYPE	COMPOUND	ANALYSIS (%)			
		LA MATONA SPAIN	EL BATÁN SPAIN	POLAND	SLOVENIA
ME-XRF30	La ₂ O ₃	<0.01	<0.01	0.01	0.01
ME-XRF30	CeO ₂	0.01	0.01	0.02	0.03
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	0.01	0.02
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	0.01	0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	0.01	0.02
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	0.01	0.01

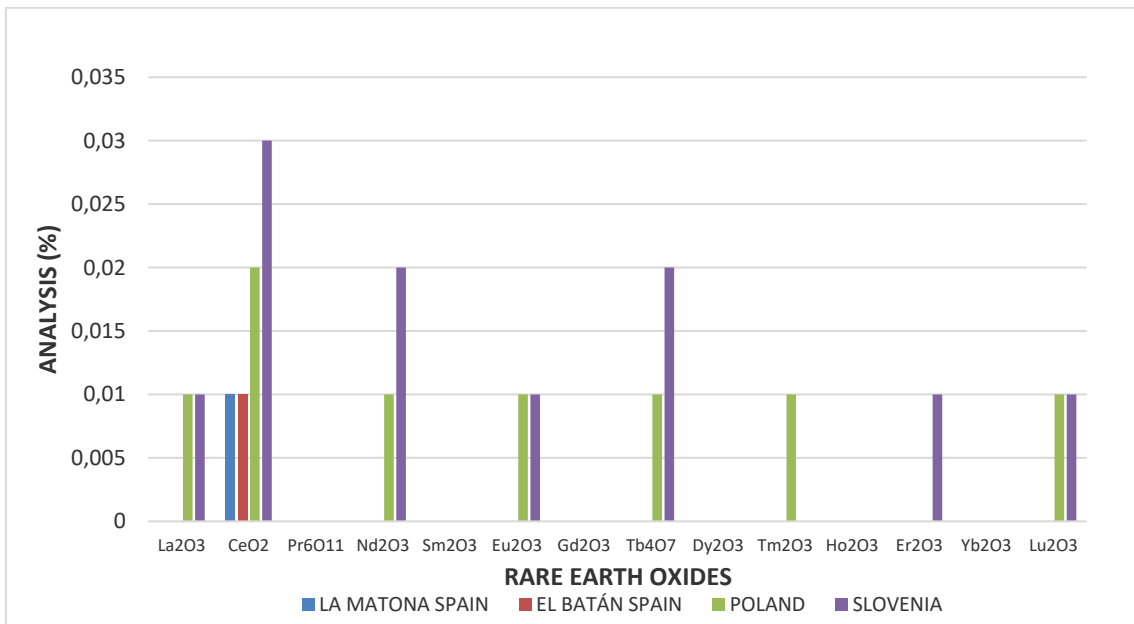


Figure 3-3. Graph of the percentage of initial analysis of oxides of rare earths

4. Granulometric separation of samples by sieving

The samples shall first be divided into different particle size fractions >2.0 mm, 2.0/0.5 mm, 0.5/0.1 mm, <0.1 mm, because these are the sizes that would be obtained at various process points in the coal washing plant. Subsequently, laboratory analysis will be developed for each fraction to identify rare earth contents and the mineralogical species present. The methods will be, e.g., Inductively Coupled Plasma-Atomic Emission Spectrometers (ICP-AES) and X-Ray Fluorescence (XRF).

With the data obtained, rare earth release and concentration analyses will be carried out to decide the particle sizes that will allow a higher recovery of rare earths.

The dry material that had been prepared for the analysis of the previous section and that had passed through the jaw crusher and the disc mill has been taken.

The machines used are the following:

- Disc mill.
- Sieve shaker with 0.1 mm, 0.5 mm and 2 mm sieves (Figure 4-1).
- Scales.



Figure 4-1. Sieve

Initially, the machines to be used must be cleaned in order to eliminate any impurities that may exist from previous procedures that could contaminate the samples. The sample is passed through the disk mill again with the minimum opening in order to reduce its grain size as much as possible.

Next, the sieves are placed in order from the smallest to the largest mesh opening, from bottom to top, and an adequate amount of material is placed on the top sieve (2 mm)

by running the sieve shaker for 10 minutes until it separates well. the fractions of <0.1 mm, from 0.1 to 0.5 mm and from 0.5 to 2.0 mm.

Once the sieve shaker stops, the different fractions obtained are placed in a properly labeled bag, repeating the operation until the entire sample is finished. From that bag the necessary material for the analysis of rare earths will be obtained.

4.1. Sieving of the La Matona sample (Spain)

We proceeded to sift the material from the La Matona sample, which was in the tray that had previously dried and had previously been passed through the disc mill (Figure 4-2).



Figure 4-2. Sample of La Matona next to the siever

The procedure required a time of 5 hours to achieve the separation by size of the entire sample of La Matona. 15 284.5 g of material have been sieved, obtaining the different granulometric fractions that are detailed in Table 4-1 and can be seen in Figure 4-3.

Table 4-1. Granulometric fractions of the La Matona sample

SIEVE (mm)	WEIGHT (g)	SAMPLE		REMAINING WEIGHT (g)
		WEIGHT (g)	NAME	
2.0 – 0.5	5935.0	200.0	MT-1	5735.0
0,5 – 0.1	4149.2	200.0	MT-2	3949.2
<0.1	1518.3	200.0	MT-3	1318.3
Rejection >2.0	3682.0	0.0	-	3682.0
TOTAL	15284.5	600.0	-	14684.5



Figure 4-3. Sieve granulometric fractions, >2.0 mm (upper left), 2.0-0.5 mm (upper right), 0.5-0.1 mm (lower left), and <0.1 mm (lower right)

Figure 4-4 shows visually the proportion of different fractions obtained by the sieving process and sampled for ash and rare earth analysis.

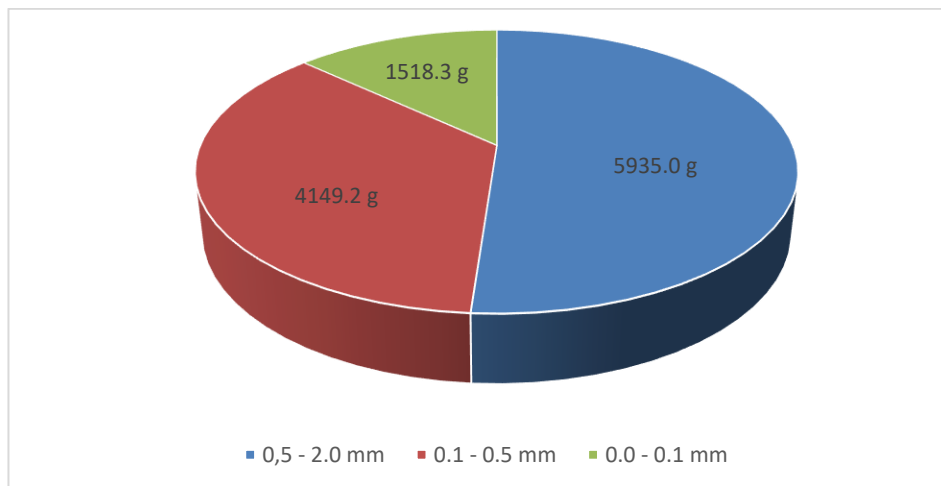


Figure 4-4. Sectorial graph of the different fractions of the sieved La Matona sample.

A sample of 200 g was taken from each of the fractions, except the rejection fraction, to carry out the rare earth analyzes of the previous section, in the accredited laboratory,

for each granulometric fraction obtained. Figure 4-5 shows the 200 g samples, duly labelled, to carry out the analysis of rare earths.



Figure 4-5. Samples for rare earth analysis

4.2. Sieving of the El Batán sample (Spain)

We proceeded to sift the material from the El Batán sample, which was in the tray that had previously dried and had previously been passed through the disc mill (Figure 6 5).



Figure 4-6. Sample of El Batán next to the sieve

The procedure required a time of 6.5 hours to achieve the separation by size of the entire sample from El Batán. 19739.0 g of material have been sieved, obtaining the different granulometric fractions that are detailed in Table 4-2 and can be seen in Figure 4-7

Table 4-2. Granulometric fractions of the El Batán sample

SIEVE(mm)	WEIGHT (g)	SAMPLE		REMAINING WEIGHT (g)
		WEIGHT (g)	NAME	
2.0 – 0.5	8106.4	200.0	B-1	7906.4
0.5 – 0.1	4148.0	200.0	B-2	3948.0
<0.1	823.3	200.0	B-3	623.3
Rejection >2.0	6661.3	0.0	-	6661.3
TOTAL	19739.0	600.0	-	19139.0



Figure 4-7. Sieve granulometric fractions, >2.0 mm (upper left), 2.0-0.5 mm (upper right), 0.5-0.1 mm (lower left), and <0.1 mm (lower right)

Figure 4-8 shows visually the proportion of different fractions obtained by the sieving process and sampled for ash and rare earth analysis.

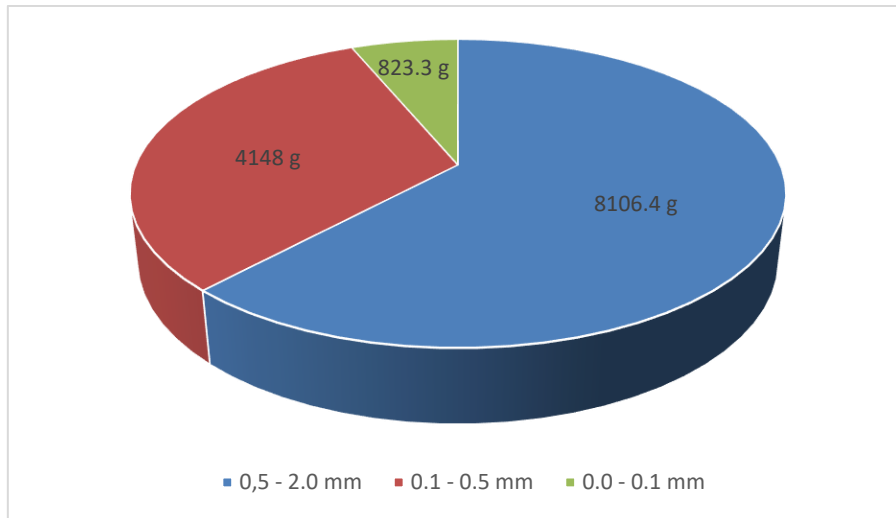


Figure 4-8. Sectorial graphic of the different granulometric fractions of the sieved sample from El Batán

A sample of 200 g was taken from each of the fractions, except the rejection fraction, to carry out the rare earth analysis of the previous section, in the accredited laboratory, for each granulometric fraction obtained. Figure 4-9 shows the 200 g samples, duly labelled, to carry out the analysis of rare earths.



Figure 4-9. Samples for rare earth analysis

4.3. Sieving of the Polish sample

The material was sieved from the Polish sample, which had previously been passed through the disc mill.

The procedure required a time of 5 hours to achieve the separation by size of one of the bags of the Polish sample. A total of 10000 g of material was sieved, obtaining the different granulometric fractions detailed in Table 4-3 and shown in Figure 4-10.

Table 4-3. Particle size fractions of the Polish sample

SIEVE (mm)	WEIGHT (g)	SAMPLE		REMAINING WEIGHT (g)
		WEIGHT (g)	NAME	
2.0 – 0.5	4599.3	50.0	PT-1	4549.3
0.5 – 0.1	2245.0	50.0	PT-2	2195.0
<0.1	1145.4	50.0	PT-3	1095.4
Rejection >2.0	2010.3	0.0	-	2010.3
TOTAL	10000.0	150.0	-	9850.0



Figure 4-10. Particle size fractions in the sieves, >2.0 mm (left), 2.0-0.5 mm, 0.5-0.1 mm and <0.1 mm (right)

Figure 4-11 shows visually the proportion of different fractions obtained by the sieving process and sampled for ash and rare earth analysis.

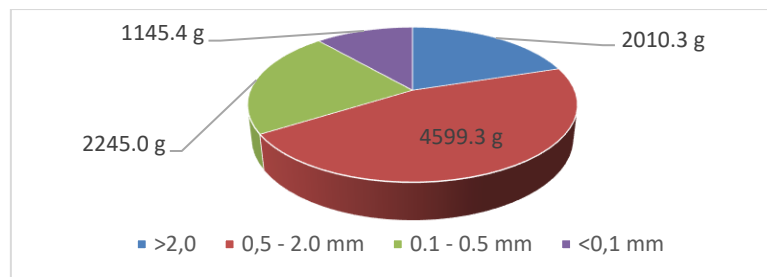


Figure 4-11. Sectoral chart of different fractions of sieved sample from Poland

A sample of 5 g was taken from each of the fractions, except for the rejection, to carry out the rare earth analyses in the previous section, in the accredited laboratory, for each granulometric fraction obtained. Figure 4-12 shows the 50 g samples, duly labelled, for the rare earth analysis.



Figure 4-12. Samples for rare earth analysis

4.4. Sieving of the Slovenian sample

The material from the Slovenian sample was sieved. The procedure required a time of 7 hours to achieve the size separation of one of the bags of the Slovenian sample. A total of 5000 g of material was sieved, obtaining the different granulometric fractions which are detailed in Table 4-4 and can be seen in Figure 4-13.

Table 4-4. Grain size fractions of the Slovenian sample

SIEVE (mm)	WEIGHT (g)	SAMPLE		REMAINING WEIGHT (g)
		WEIGHT (g)	NAME	
2.0 – 0.5	695.5	50.0	PT-1	645.5
0.5 – 0.1	1583.2	50.0	ST-2	1533.2
<0.1	1374.9	50.0	ST-3	1324.9
Rejection >2.0	1346.4	-	-	1346.4
TOTAL	5000.0	150.0	-	4850.0



Figure 4-13. Particle size fractions in the sieves, >2.0 mm (left), 2.0-0.5 mm, 0.5-0.1 mm and <0.1 mm (right)

In Figure 4-14 the proportion of different fractions obtained by the sieving process and sampled for ash and rare earth analysis can be seen visually.

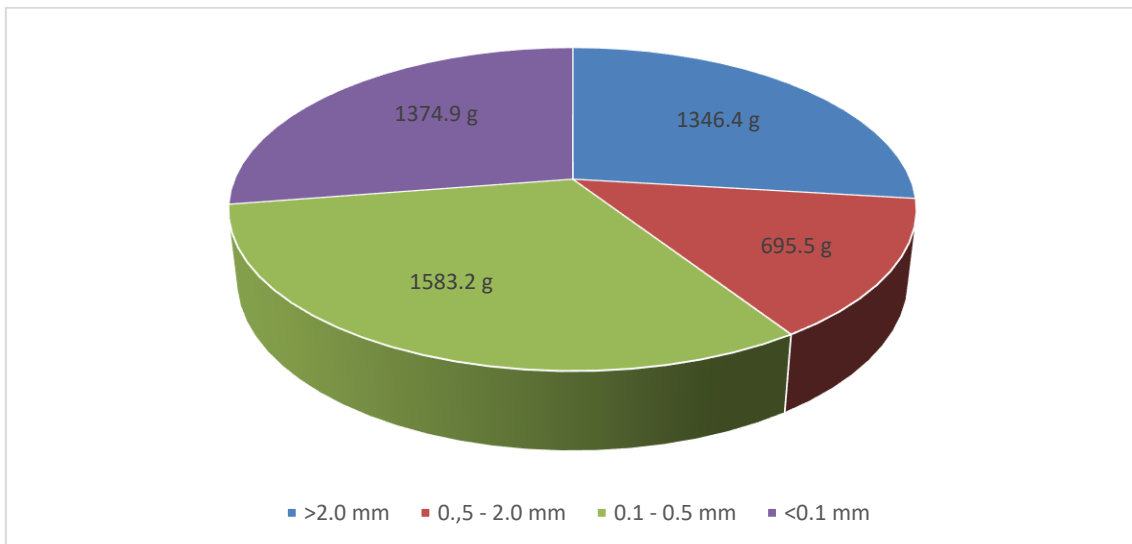


Figure 4-14. Sector chart of different fractions of sieved sample from Slovenia

A sample of 5 grams was taken from each of the fractions, except for the rejection, to carry out the rare earth analyses in the previous section, in the accredited laboratory, for each granulometric fraction obtained. Figure 4-15 shows the 50 g samples, duly labelled, for the rare earth analysis.



Figure 4-15. Samples for rare earth analysis

5. Analysis of sieved separated samples

This section presents the results of the analysis of the samples from Spain (La Matona and El Batán), Poland and Slovenia carried out in the accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and a percentage analysis of other elements and their oxides (%) called ME_XRF30 had been requested from the documentation provided by the laboratory. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

The results of the quantitative analysis in parts per million obtained from the sieved samples are shown in Table 5-1, as well as in the graph in Figure 5-1.

Table 5-1. Results of quantitative analysis (ppm) of elements in sieved samples

TYPE	ELEMENT	LA MATONA-SPAIN			EL BATÁN-SPAIN			POLAND			SLOVENIA		
		M_2,0-0,5mm	M_0,5-0,1mm	M_0,1-0,0mm	B_2,0-0,5mm	B_0,5-0,1mm	B_0,1-0,0mm	P_2,0-0,5mm	P_0,5-0,1mm	P_0,1-0,0mm	S_2,0-0,5mm	S_0,5-0,1mm	S_0,1-0,0mm
-	Sc	20.00	20.00	20.00	2.70	5.10	6.10	20.00	20.00	20.00	20.00	20.00	20.00
-	Y	26.30	23.40	30.60	1.50	2.20	6.50	30.30	27.70	31.60	34.60	35.40	27.70
LREE	La	38.30	32.60	35.40	31.40	25.00	26.00	29.00	26.30	29.80	33.60	35.50	27.70
	Ce	78.50	68.30	73.80	67.30	52.60	55.70	63.50	57.50	63.00	68.1	71.00	56.60
	Pr	9.16	8.20	8.77	18.00	19.80	26.40	4.18	7.13	7.77	8.19	8.60	6.89
	Nd	34.00	30.20	33.50	11.90	10.00	10.20	28.50	25.70	30.00	33.50	33.80	27.40
MREE	Sm	6.29	5.54	6.37	<3	5.00	<3	7.11	6.22	6.51	6.78	7.84	5.86
	Eu	1.38	1.00	1.26	1.12	1.91	0.87	1.72	1.50	1.56	2.00	1.88	1.48
	Gd	5.53	4.94	5.60	4.32	3.84	3.93	5.45	5.50	6.26	6.11	6.42	5.24
HREE	Tb	0.86	0.67	0.96	0.77	0.63	0.61	0.90	0.97	0.97	1.06	1.15	0.89
	Dy	4.53	4.00	5.10	3.33	2.98	3.22	6.32	5.31	6.16	6.15	6.30	5.31
	Ho	0.95	0.80	1.11	0.73	0.63	0.68	1.10	0.93	1.03	1.10	1.18	0.89
	Er	2.67	2.22	2.97	1.93	1.71	0.99	3.73	3.01	3.38	3.09	3.22	2.64
	Tm	0.37	0.34	0.47	0.63	0.45	0.46	0.41	0.39	0.46	0.47	0.59	0.39
	Yb	2.77	2.21	3.02	19.20	16.90	18.70	2.83	2.42	3.27	3.06	2.98	2.46
	Lu	0.37	0.32	0.42	0.30	0.22	0.27	0.49	0.39	0.34	0.40	0.40	0.30
TOTAL		231.98	204.74	229.35	165.13	148.97	160.63	205.54	190.97	212.11	228.21	236.26	191.75

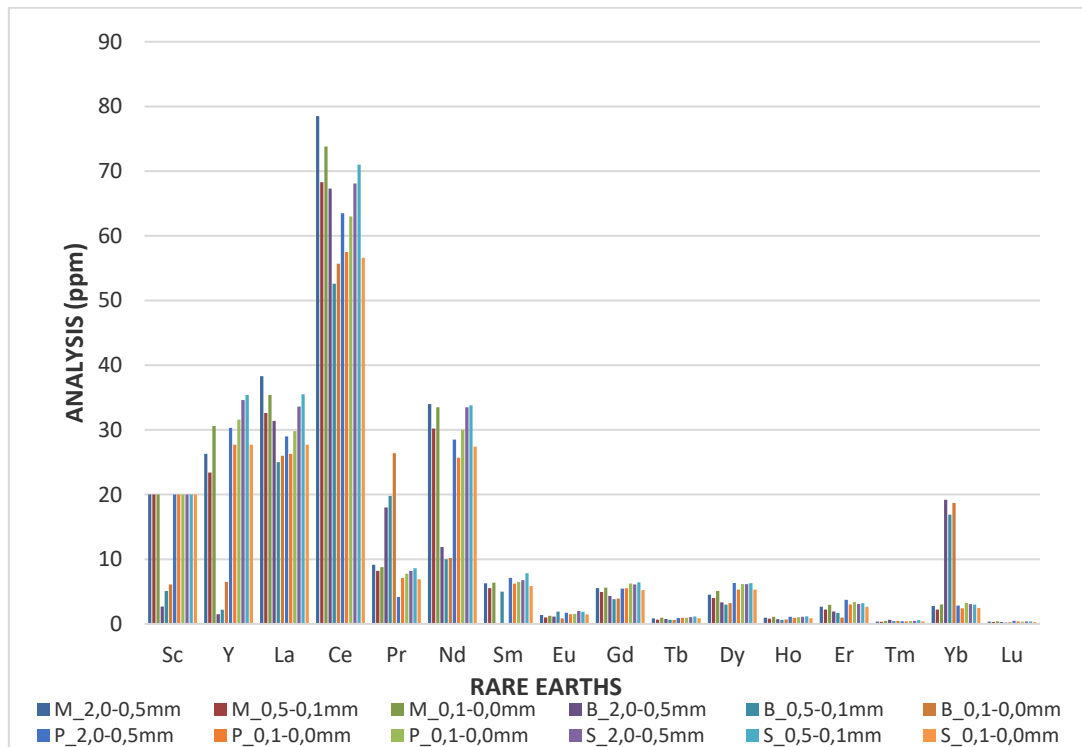


Figure 5-1. Graph of the quantitative analysis (ppm) of elements in the samples

By independently analysing the different types of rare earths, i.e. Sc-Y, light rare earths (LREE), medium rare earths (MREE) and heavy rare earths (HREE), a more appropriate partial view can be obtained with the different scales of values present.

Figure 5-2 shows the comparative results of the quantitative analysis (ppm) of the samples from Spain, Poland and Slovenia. It can be seen that the Scandium (Sc) content is similar in the four samples, being around 20 ppm except in the sample from El Batán where it is between 2.7 and 6.1 ppm. The Itrium (Y) content varies depending on the granulometry between 23.4 and 35.4 ppm, except in the El Batán sample, where the content is very low, as is the case with Scandium, which may be due to the higher carbon content present in the sample.

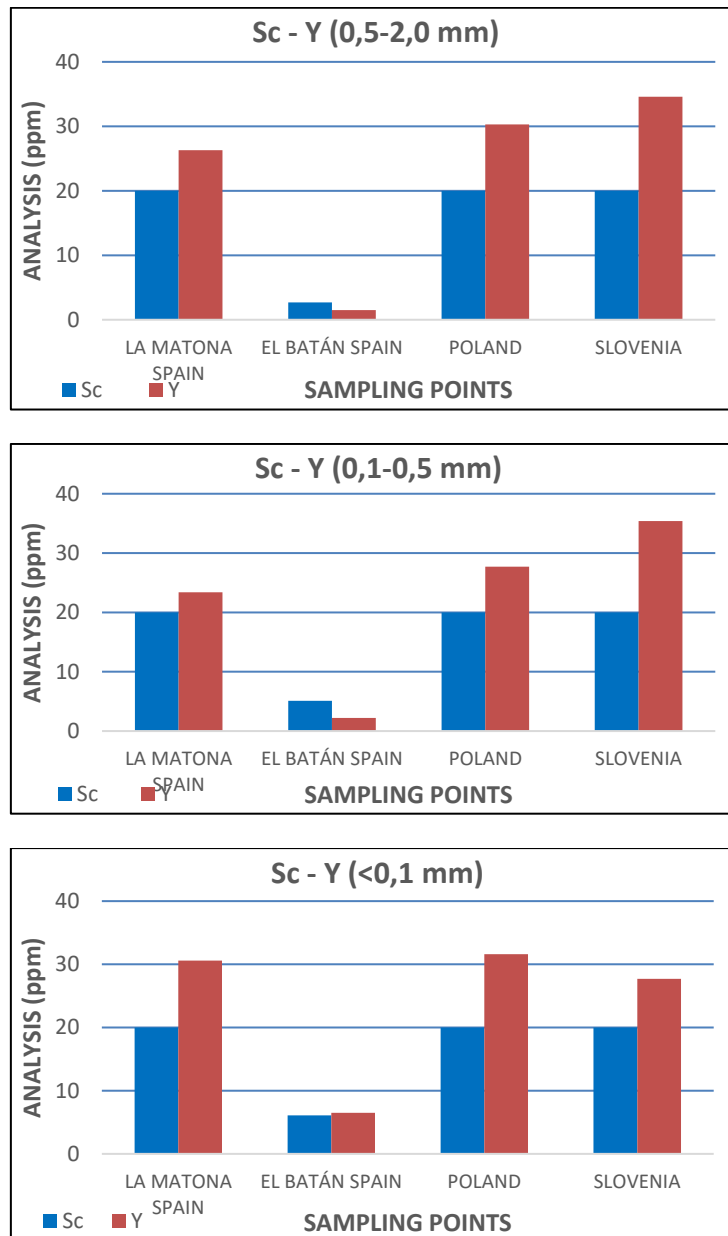


Figure 5-2. Comparison of the Sc-Y element contents (ppm) of the sieved samples at all sampling points.

Figure 5-3 shows a comparison of the quantitative analyses (ppm) of light rare earths (LREE) for the different granulometries resulting from the sieving. It can be seen that there are no significant variations in either the different rare earth elements or in the different sampling points, with a predominance of Cerium (Ce) in the four samples,

which exceeds 70 ppm, compared to the other elements of the group, which are all concentrated below 40 ppm.

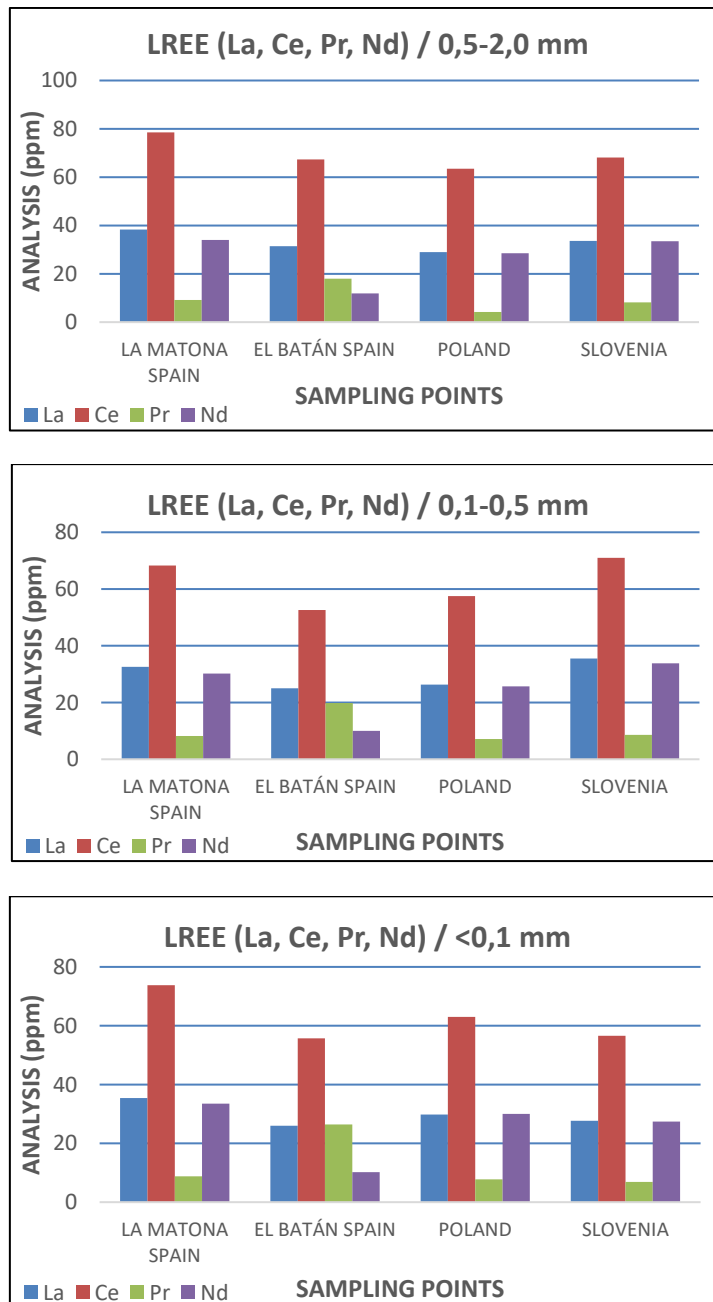


Figure 5-3. Comparison of the ppm content of light rare earths (LREE), La, Ce, Pr and Nd in sieved samples and at all sampling points.

Figure 5-4 shows a comparison of the quantitative analyses (ppm) of mean rare earths (MREE) for the different particle sizes resulting from the sieving. It can be seen that the

concentrations of Samarium (Sm) and Gadolinium (Gd) are higher than that of Europium (Eu) and better at the end grain sizes than in the middle.

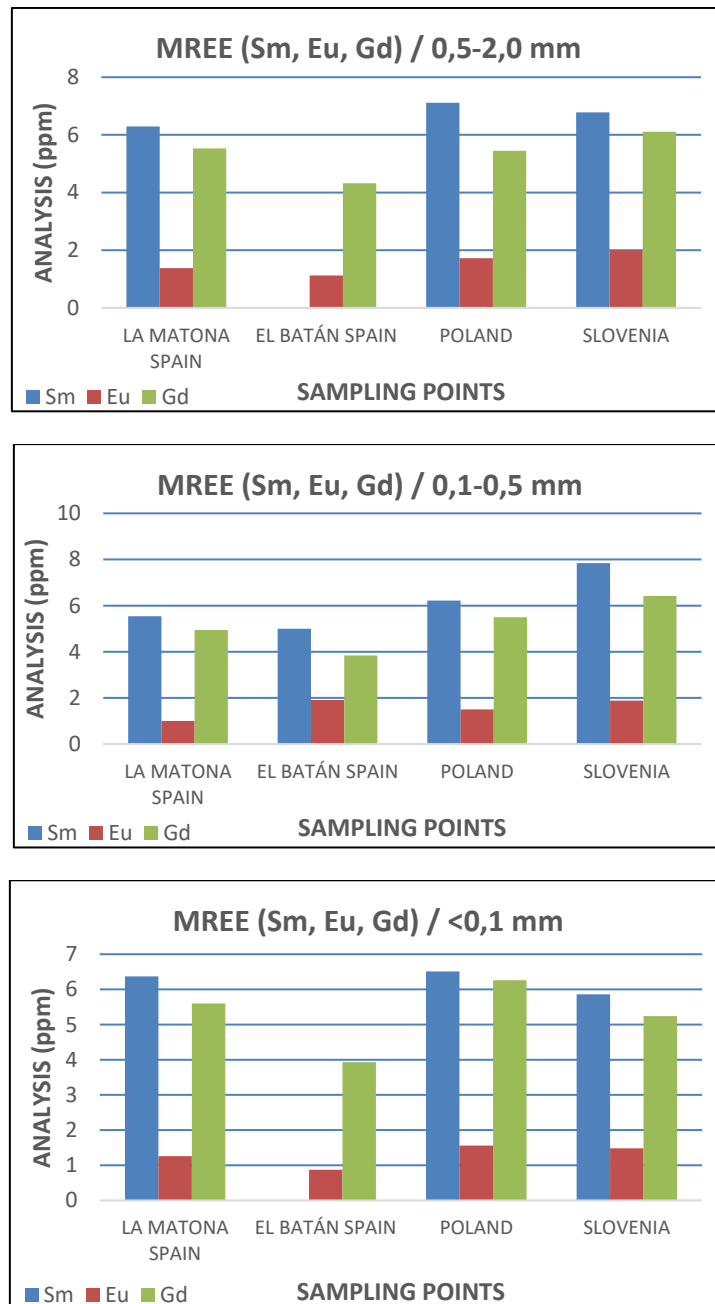


Figure 5-4. Comparative ppm content of mean rare earths (MREE), Sm, Eu and Gd of sieved samples and at all sampling points

Figure 5-5 shows a comparison of the quantitative analyses (ppm) of heavy rare earths (HREE) for the different granulometries resulting from the sieving. It can be seen that Lutetium (Lu) is higher than the other elements in the El Batán sample, exceeding 18

ppm, while the other elements do not exceed 7 ppm. There are no notable differences in the concentrations of the elements between the different sampling points.

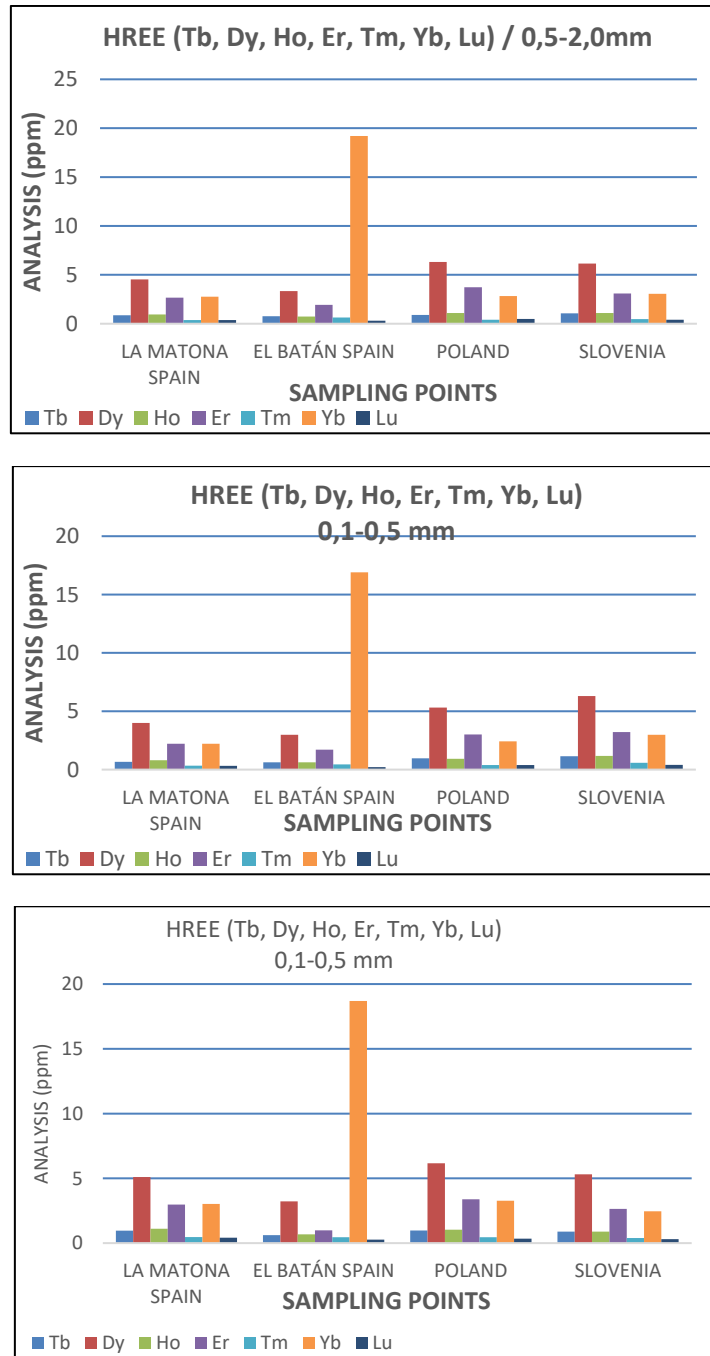


Figure 5-5. Comparative ppm content of heavy rare earths (HREE), Tb, Dy, Ho, Er, Tm, Yb and Lu of sieved samples and at all sampling points.

The results of the percentage analysis obtained from the sieved samples are shown in Table 5-2, as well as in the graph in Figure 5-6. No significant variations are observed

neither between the different particle sizes nor between the different sampling points, with most of the analyses being below the detection limit.

Table 5-2. Results of the percentage analysis of oxides of rare earths in the sieved samples

METHOD	COMPOUND	LA MATONA SPAIN (%)			EL BATÁN SPAIN (%)			POLAND (%)			SLOVENIA (%)		
		M_2,0-0,5mm	M_0,5-0,1mm	M_0,1-0,0mm	B_2,0-0,5mm	B_0,5-0,1mm	B_0,1-0,0mm	P_2,0-0,5mm	P_0,5-0,1mm	P_0,1-0,0mm	S_2,0-0,5mm	S_0,5-0,1mm	S_0,1-0,0mm
ME-XRF30	La ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	0.01	0.01	0.01
ME-XRF30	CeO ₂	0.01	0.01	0.01	0.01	0.01	<0.01	0.02	0.02	0.02	0.02	0.03	0.02
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.02	0.02	0.02
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.01	0.01	0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.02	0.02	0.02	0.01
ME-XRF30	Tm ₂ O ₃	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	<0.01	<0.01	0.01

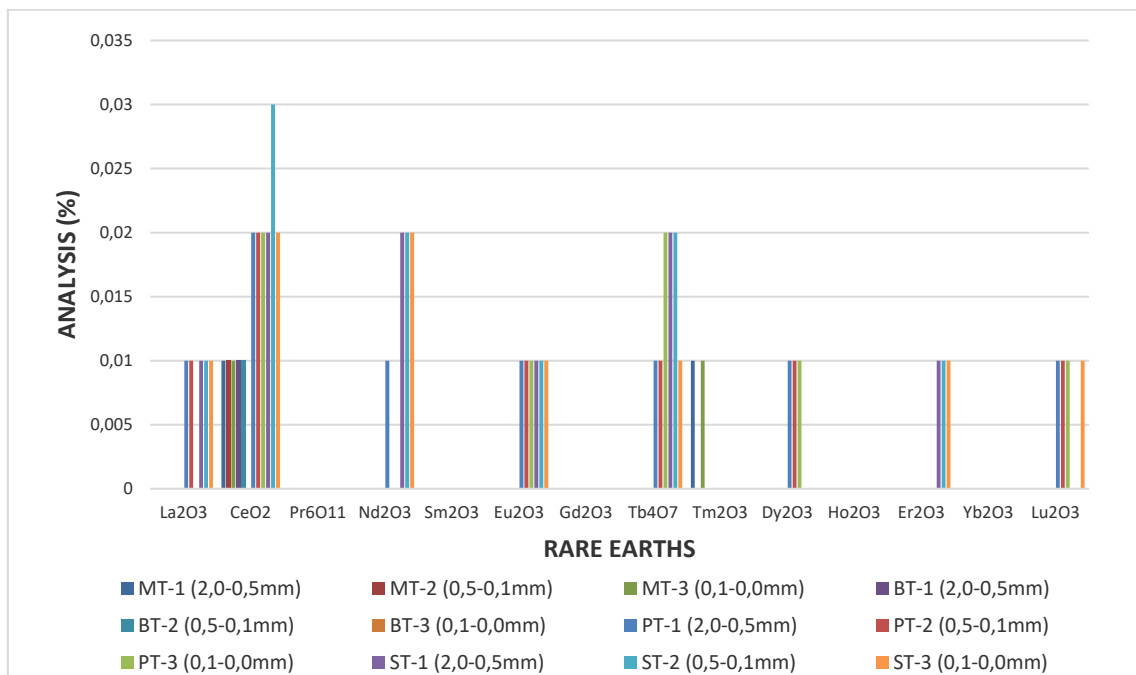


Figure 5-6. Graph of the results of the percentage analysis of oxides of rare earths in samples

Four groups of results are differentiated in all the sampling points: the first the oxides whose result is below the detection limit, the second 9 oxides whose result is 0.01%, the third is the result of 0.02% (CeO_2 , Nd_2O_3 and Tb_4O_7) and finally the result of 0.03% which was only reached by CeO_2 in the 0.1-0.5 mm grain size subsample from Slovenia.

Since the analyses performed, both the initial ones and those of the screened samples, show very similar rare earth concentrations in the three countries considered (Figure 5-1), in order to fit the available budget and to perform as many concentration tests as possible by different test methods, the possibilities of rare earth concentration in the two Spanish samples will be studied in detail, since one of them comes from a landfill and the other from a laundry, the latter showing a significant carbon content.

The results are expected to be mostly extrapolated from one waste to another.

6. Pulsation box or hydraulic screen (jig)

Since almost all rare earth minerals are very dense, gravimetric concentration analysis will be developed in the first place to obtain a dense wet concentrate. The equipment to be used will depend on the liberation analysis: multigravity separator for sizes <0.1 mm, shaking tables for sizes between 0.1 and 0.5 mm, and pulsation box for sizes between 0.5 and 2.0 mm. Here we will analyse the pulsation box.

The pulsation box separator is based on the principle of concentration by differential acceleration and consists of a box with a fixed screen, in which the pulsation is carried out by a diaphragm or piston. The pulsations are caused by eccentrics that act on each particle with a double acceleration, which generates a separation in the fluid medium.

A pulsation box is an easy-to-assemble device that only requires a few water and electricity supplies for its correct operation. The control of the water flow and water supply is very important in order to obtain maximum efficiency in the process and in production, as it is not the same for the different materials to be treated.

The water supplied to the equipment through different inlets generates a fluid bed where the separation takes place according to its density, with the less dense materials remaining in the upper part of the bed and those with a higher density in the lower part.

6.1. Procedure for the separation of samples by pulsation box

This section will describe the densitometrically separation procedure of the samples for analysis in an accredited laboratory. The machines used are the following:

- Jig (Figure 6-1, left)
- Stove (Figure 6-1, right)
- Scale



Figure 6-1. Pulsation box (jig) and Stove

The pulsation box separation equipment is based on the principle of concentration by differential acceleration and is made up of a box with a fixed screen, in which the pulsation is carried out with a diaphragm or piston. The pulsations are caused by eccentrics that cause a double acceleration to act on each particle, which generates a separation in the fluid medium.

A pulsation box is an easy to assemble piece of equipment that only requires water and electricity supplies to allow it to function correctly. The control of the flow and supply of water is very important when it comes to obtaining maximum efficiency in the process and in production, and it is not the same for the different materials to be treated.

The water supplied to the equipment by different intakes generates a fluid bed where the separation takes place according to its density, leaving less dense materials in the upper part of the bed and those with a higher density in the lower part.

Initially, the machine to be used must be cleaned in order to eliminate any impurities that may exist from previous procedures that could contaminate the samples.

The dry material, 2.0 – 0.5 mm in size, which had been previously prepared, was taken. Said material is introduced into the cylinder with the piston low, which contains water, and the equipment is put to work for 5 minutes. The pulsations that are generated in that time originate the separation by density.

Once the process is finished, the piston is raised and the different sheets of material are removed, with different densities, to the duly labelled trays for subsequent drying in the oven at a temperature of 100°C (Figure 6-2).



Figure 6-2. Trays with different densities inside the stove

When all the material is in the oven, the water is removed from the pulsation box at the bottom, it is cleaned well and it is filled with water, placing the piston low to carry out the process again with another sample.

6.2. Sample of La Matona (Spain)

947.10 grams of material from La Matona with a grain size between 0.5 and 2.0 mm were used and passed through the pulsation box. After 5 minutes, the particles were separated according to their density. Five densitometrically different subsamples were separated and dried in the oven to obtain the weights shown in Table 6-1 and visually in Figure 6-3. Subsequently, 20 grams of each subsample were taken for rare earth analysis in an accredited laboratory and 5 grams of each for ash analysis.

Table 6-1. Densitometrically distinct sub-samples of the La Matona sample

SAMPLE	WEIGHT (g)
MP-1	62.0
MP-2	196.1
MP-3	226.5
MP-4	254.1
MP-5	208.4
TOTAL	947.1

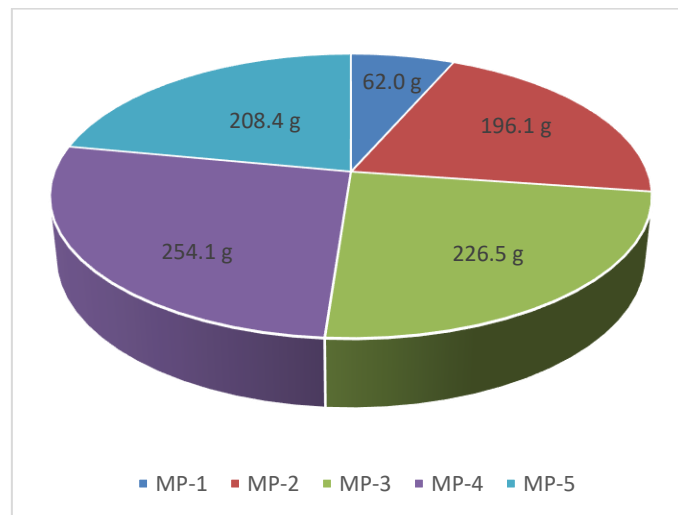


Figure 6-3. Graph of subsamples obtained in the pulse box of La Matona sample.

6.3. Sample of El Batán (Spain)

808.40 grams of material from El Batán with a grain size between 0.5 and 2.0 mm were used and passed through the pulsation box. After 5 minutes, the particles were separated according to their density. Five densitometrically different subsamples were separated, which were dried in the oven to obtain the weights shown in Table 6-2 and

visually in Figure 6-4. Subsequently, 20 grams of each subsample were taken for rare earth analysis in an accredited laboratory and 5 grams of each for ash analysis.

Table 6-2. Desymmetrically distinct sub-samples of the El Batán sample

SAMPLE	WEIGHT (g)
BP-1	155.5
BP-2	112.5
BP-3	184.8
BP-4	223.7
BP-5	131.9
TOTAL	808.4

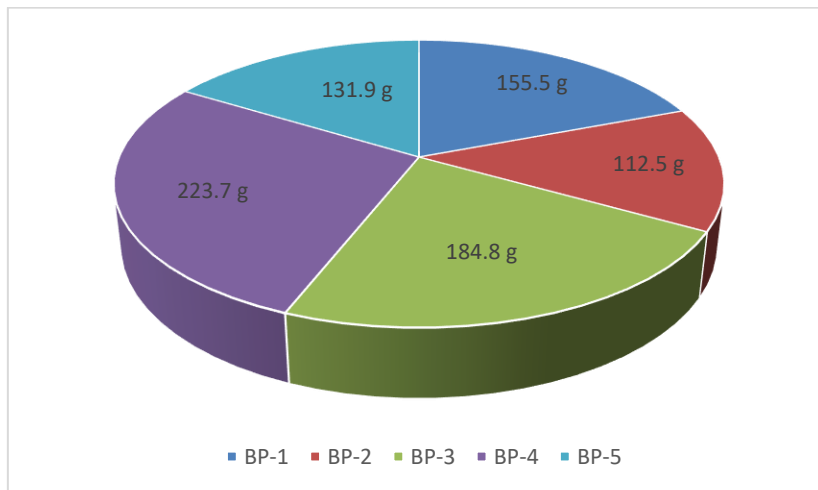


Figure 6-4. Graph of the sub-samples obtained in the pulse box of El Batán sample.

7. Analysis of density-separated samples using the pulse box or hydraulic sieve method

This section presents the results of the analysis of the samples from La Matona and El Batán carried out in an accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and a percentage analysis of other elements and their oxides (%) called ME_XRF30, from the documentation provided by the laboratory, had been requested. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

With the data obtained, rare earth release and concentration analyses will be carried out to decide the particle sizes that will allow a higher recovery of rare earths.

¡Error! No se encuentra el origen de la referencia. shows the quantitative analysis results in parts per million (ppm) obtained from the sieved samples from La Matona and El Batán. These data can be seen graphically in Figure 7-1 and Figure 7-2. Analysing the result shows a higher concentration of the light rare earth (LREE) elements which remain below 25 ppm except for Yttrium (Y), Lanthanum (La), Cerium (Ce) and Neodymium (Nd) which are more concentrated reaching values between 35 and 88 ppm in the La Matona sample and between 27 and 102 ppm in the El Batán sample.

Table 7-1. Results of the quantitative analysis (ppm) of elements in the samples from the pulsation box.

METHOD	ELEMENT	SAMPLES (ppm)									
		MATONA					EL BATÁN				
		MP-1 (- dense)	MP-2	MP-3	MP-4	MP-5 (+ dense)	BP-1 (- dense)	BP-2	BP-3	BP-4	BP-5 (+ dense)
ME-MS89L	Sc	20.00	20.00	20.00	20.00	20.00	10.00	20.00	30.00	20.00	20.00
ME-MS89L	Y	14.40	27.20	28.20	28.40	28.10	7.50	15.60	24.30	27.00	26.30
ME-MS89L	La	16.80	39.00	40.90	39.70	39.40	4.27	17.75	41.10	47.00	45.30
ME-MS89L	Ce	37.50	83.70	87.40	86.80	85.90	9.70	39.20	86.50	102.00	98.80
ME-MS89L	Pr	4.28	9.47	9.74	9.61	9.41	1.28	4.64	9.62	11.45	11.10
ME-MS89L	Nd	16.10	35.40	36.40	37.20	36.30	5.79	17.85	37.00	42.10	41.30
ME-MS89L	Sm	3.44	7.16	7.66	6.93	8.59	1.41	3.79	6.53	8.56	8.61
ME-MS89L	Eu	0.78	1.42	1.40	1.42	1.37	0.31	0.77	1.53	1.67	1.63
ME-MS89L	Gd	2.90	5.24	5.91	5.70	5.74	1.58	3.17	4.98	5.69	5.98
ME-MS89L	Tb	0.50	0.86	0.92	0.86	0.91	0.22	0.46	0.71	0.94	0.91
ME-MS89L	Dy	2.36	4.83	4.95	5.04	5.29	1.71	2.76	4.05	5.00	4.79
ME-MS89L	Ho	0.46	0.93	1.01	0.98	1.06	0.27	0.50	0.78	0.96	0.99
ME-MS89L	Er	1.32	2.85	2.99	3.01	2.91	0.73	1.52	2.39	3.11	2.70
ME-MS89L	Tm	0.19	0.36	0.40	0.45	0.37	0.09	0.23	0.36	0.41	0.40
ME-MS89L	Yb	1.46	2.67	2.74	2.66	2.67	0.59	1.26	2.49	2.70	2.91
ME-MS89L	Lu	0.14	0.38	0.42	0.35	0.36	0.08	0.20	0.40	0.41	0.35
TOTALES		122.63	241.47	251.04	249.11	248.38	45.53	129.70	252.74	279.00	272.07

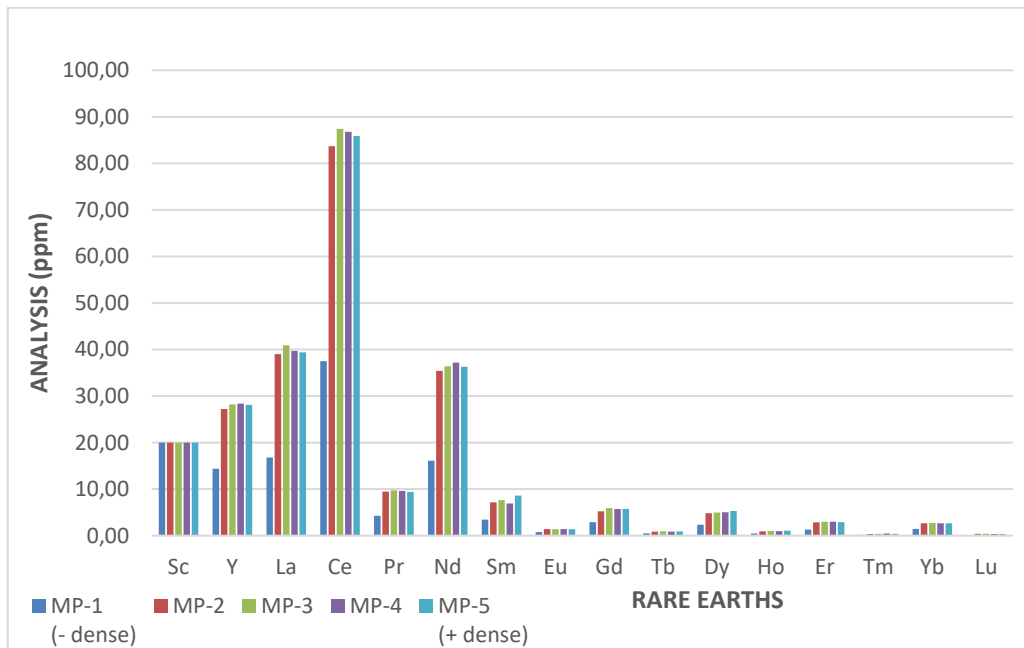


Figure 7-1. Graph of the quantitative analysis of the samples from La Matona using the pulse box

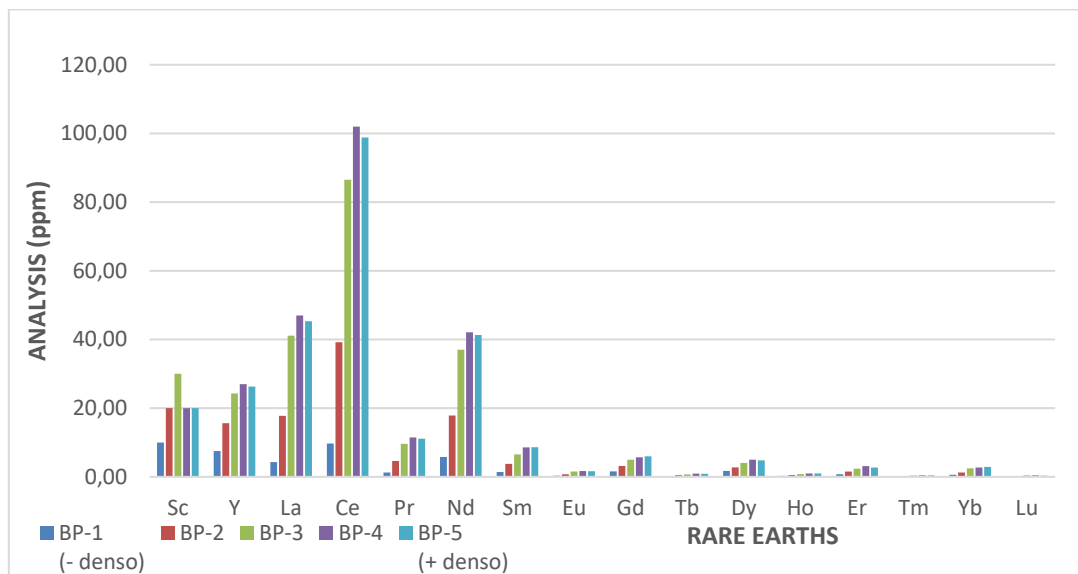


Figure 7-2. Graph of the quantitative analysis of the samples from El Batán using the pulse box

In the upper left graph of Figure 7-3 no significant variations are observed in the densitometric concentrations of Scandium (Sc) and Yttrium (Y) in both samples except for an increase in the higher density subsamples. In the lower density subsample (P-1) a lower concentration is evident, especially in the sample from El Batán, due to the higher amount of carbon it contains.

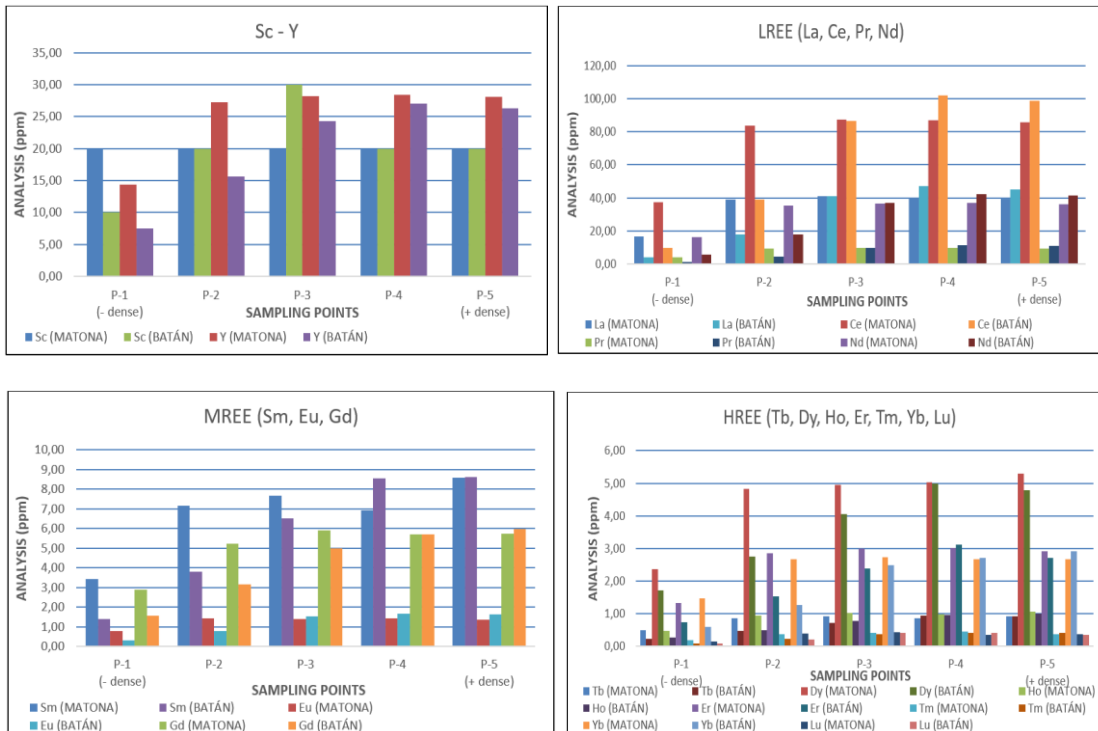


Figure 7-3. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) using the pulse box

The top right graph shows the LREE results. It can be seen that the Cerium (Ce) content is much more abundant than the rest of the elements of this group in all the samples. No significant variations are observed in the LREE group.

The bottom left graph shows the results of the MREE analysis. The concentration of Samarium (Sm) is somewhat higher in La Matona sample than in El Batán sample in the second, lower density sub-sample. The remaining elements have insignificant variations in concentration except that they increase with density.

The lower right graph shows the results of the HREE analysis. The concentration of Dysprosium (Dy), Erbium (Er) and Ytterbium (Yb) are much higher than the rest of elements.

The results of the percentage analysis obtained from the samples obtained from the pulsation box of La Matona and El Batán are shown in **¡Error! No se encuentra el origen de la referencia.**, as well as in the graphs in Figure 7-4 (La Matona) and Figure 7-5 (El Batán). It is observed that the results are below the detection limit except for Cerium Oxide (CeO₂) which reaches a value of 0.01%, in some of the subsamples of the La Matona and El Batán pulsation box samples, and in the lower density subsample of El Batán where 0.01% of Lanthanum Oxide (La₂O₃) is concentrated.

Table 7-2. Results of the percentage analysis (%) of elements in the samples of the pulsation box

METHOD	ELEMENT	SAMPLES (%)									
		MATONA									
		MP-1 (- dense)	MP-2	MP-3	MP-4	MP-5 (+ dense)	BP-1 (- dense)	BP-2	BP-3	BP-4	BP-5 (+ dense)
ME-XRF30	La ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	CeO ₂	<0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

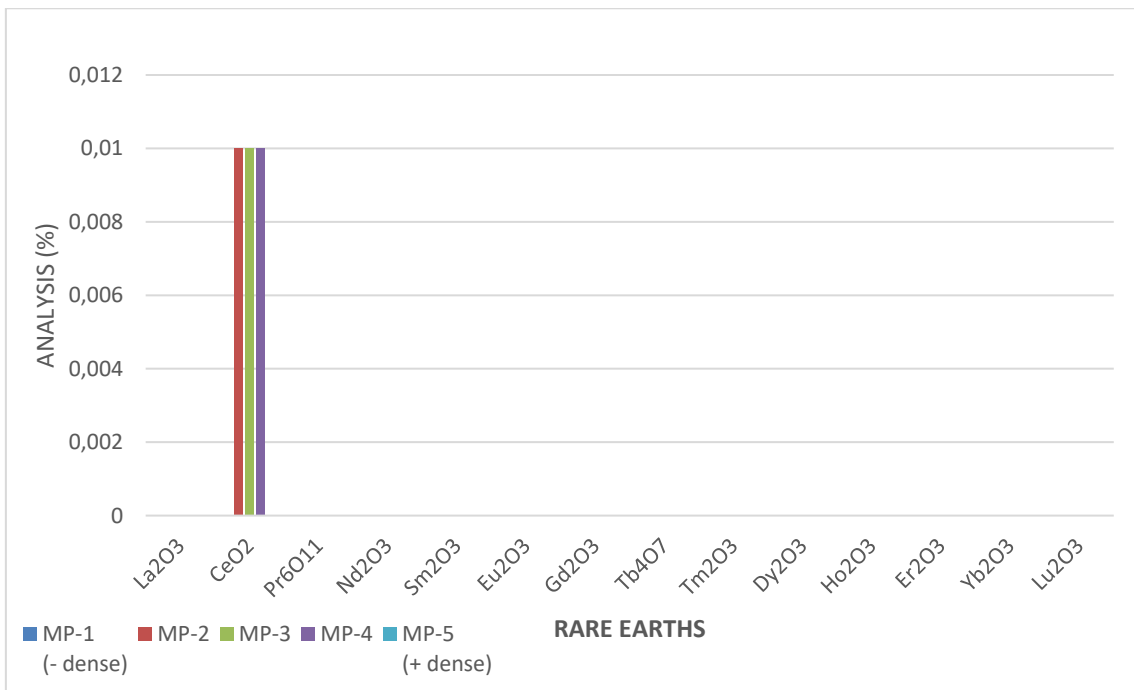


Figure 7-4. Graph of the percentage analysis of elements of the samples from La Matona obtained using the pulsation box.

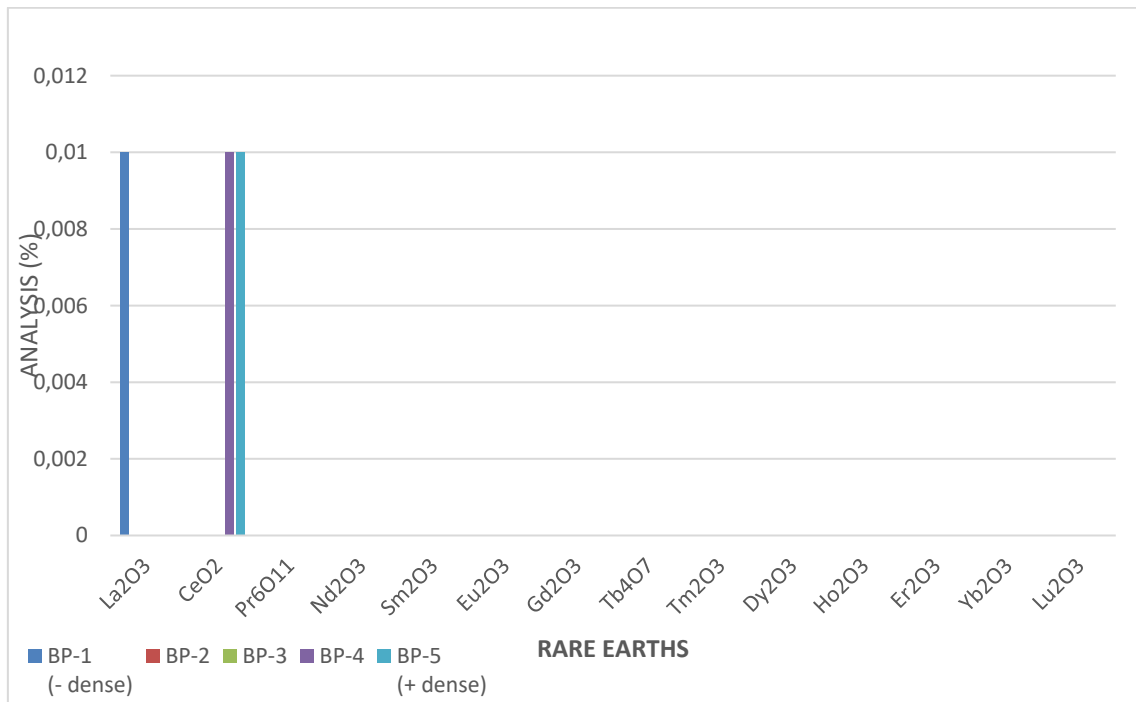


Figure 7-5. Graph of the percentage analysis of oxides of rare earths of the El Batán samples obtained using the pulsation box.

8. Magnetic field separation test

Based on the paramagnetic character of rare earth minerals, the dense concentrate will be subjected to high field strength magnetic separation, using a dry route for particle sizes >0.1 mm.

Magnetic separators take advantage of the difference in the magnetic properties of minerals. In this way, they are used to separate minerals (Table 8-1) and obtain different products classified according to their commercial importance and industrial use. Thus, separators may be used to separate a high-value magnetic product from a product considered as gangue that would be disposed of as barren (e.g. separating magnetite from quartz). Or to separate a magnetic mineral from other non-magnetic minerals (e.g. to obtain wolframite or magnetite from tin ores (cassiterite)).

Table 8-1. Magnetic intensity required (Teslas) in the separation of different magnetic minerals

MAGNETIC INTENSITY REQUIRED (TESLAS)	PROPERTY	MINERAL
0.05-0.50	Strongly magnetic	Magnetite, Franklinite, Leucite, Pyrrhotite
0.50-1.00	Moderately magnetic	Ilmenite, Biotite, Garnet, Wolframite
1.00-1.80	Weakly magnetic	Hematite, Columbite, Limonite, Limonite, Pyrolusite, Rhodochrosite, Siderite, Manganite
1.80-2.30	Poorly magnetic	Rutile, Rhodonite, Dolomite, Tantalite, Cerussite, Epidote, Monazite, Fergusonite, Zircon, Ceragirite, Argentite, Pyrite, Sphalerite, Molybdenite, Bornite, Sheelite

In general, it can be said that all substances are affected when subjected to the action of a magnetic field, however, some substances will have an effect that is too weak to be detected.

All materials can be classified according to their magnetic properties.

"Paramagnetic" minerals that are attracted to the points of highest magnetic intensity and along the lines of magnetic force. Minerals of this group can be concentrated with the use of high intensity magnetic separators. Examples of such minerals: ilmenite(FeTiO_3), rutile (TiO_2), wolframite ($(\text{Fe,Mn})\text{WO}_4$), monazite (rare earth), siderite

(FeCO_3), pyrrhotite (FeS), chromite (FeCr_2O_4), haematite (Fe_2O_3), and manganese minerals).

“Diamagnetic” minerals that will be repelled along the magnetic lines of force to those points where the magnetic field is at its lowest field strength. These substances cannot be magnetically concentrated.

“Ferromagnetic” minerals can be considered as a special category of paramagnetic materials. They exhibit very high magnetic susceptibilities within a field of magnetic forces, and retain some magnetism (remanent magnetism) once they have been taken out of the reach of the magnetic field. Such substances can be concentrated with the use of low-intensity magnetic separators. The main ferromagnetic mineral that is magnetically concentrated is magnetite (Fe_3O_4), although haematite (Fe_2O_3) and siderite (FeCO_3) can be roasted into magnetite for good separation.

In the mineral processing industry, magnets are used to remove from the flow any metallic elements that could damage equipment such as crushers, mills, etc. (Figure 8-1). They are also used as separating and concentrating units for minerals according to their magnetic susceptibility characteristics.

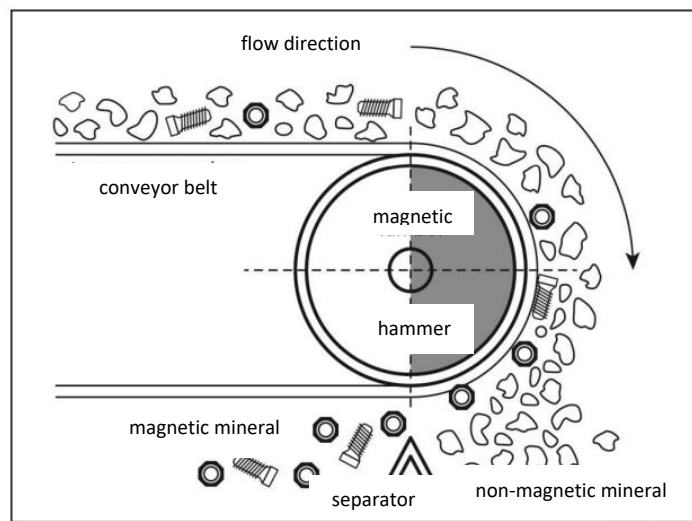


Figure 8-1. Diagram of the operation of a magnetic drum for metal removal (Fuerstenau and Han, 2003).

The magnetic separator for optimum operation allows the use of material with a particle size of 2.0-0.5 mm and with 0.1-0.5 mm.

8.1. Procedure for magnetic separation of samples

This section shall describe the procedure for magnetic separation of samples for analysis in an accredited laboratory. Two samples shall be taken from each raw sample, one

consisting of magnetic minerals and one consisting of non-magnetic minerals. The sieved material shall be used for this method at the sizes of 0,1-0,5 mm and 0,5-2,0 mm.

The machines used are as follows:

- Magnetic separator (Figure 8-2)
- Scale



Figure 8-2. Magnetic separator

Initially, the machine to be used must be cleaned in order to remove any impurities that may exist from previous procedures that could contaminate the samples. Once plugged into the mains, the machine is set to maximum magnetic induction (20000 Gauss). This is done by turning the control knob up to the 3 Ampere supply current to the coil. The roll speed is set at 20 revolutions per minute (r.p.m.).

Dry material of two different particle sizes (2.0 - 0.5 mm and 0.5 - 0.1 mm), which was prepared earlier, is taken. This material is introduced into the upper cone of the magnetic separator, sliding along the cylinder and circulating between the magnets. It can be seen how the material is separated according to its magnetic properties and falls into the two lower trays.

8.2. Sample from La Matona (Spain)

153 grams of material from La Matona with a grain size between 0.5 and 2.0 mm and 47.4 grams with a grain size between 0.1 and 0.5 mm were used.

It is observed that the sample with a grain size between 0.5 and 2.0 mm (Sample MM-1) presents 13.3% of materials with magnetic properties compared to 86.7% of non-

magnetic materials in its composition. On the other hand, the sample with a grain size between 0.1 and 0.5 mm (Sample MM-2) contains 40.3% of materials with magnetic properties versus 59.7% of non-magnetic materials as can be seen in Table 8-2 and Figure 8-3.

Table 8-2. Magnetic separation of the La Matona sample

SAMPLE	GRAIN SIZE (mm)	WEIGHT SAMPLE (mm)	SEPARATION (g)			
			MAGNETIC		NON-MAGNETIC	
			WEIGHT (g)	%	WEIGHT (g)	%
MM-1	0.5 – 2.0	153.0	20.4	13.3	132.6	86.7
MM-2	0.1 – 0.5	47.4	19.1	40.3	28.3	59.7

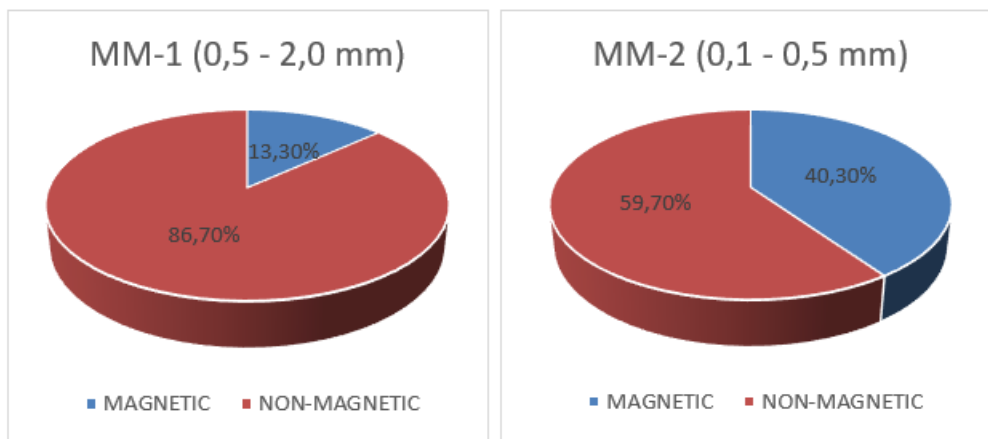


Figure 8-3. Different fractions resulting from the magnetic separator on the La Matona sample

8.3. Sample from El Batán (Spain)

We used 152.8 grams of material from El Batán with a grain size between 0.5 and 2.0 mm and 53.8 grams with a grain size between 0.1 and 0.5 mm.

It is observed that the sample with a grain size between 0.5 and 2.0 mm (Sample BM-1) presents 9.2% of materials with magnetic properties compared to 90.8% of non-magnetic materials in its composition. On the other hand, the sample with a grain size between 0.1 and 0.5 mm (Sample BM-2) contains 37.2% of materials with magnetic properties versus 62.8% of non-magnetic materials (Table 8-3 and Figure 8-4).

Table 8-3. Magnetic separation of the El Batán sample

SAMPLE	GRAIN SIZE (mm)	WEIGHT SAMPLE (mm)	SEPARATION (g)			
			MAGNETIC		NO-MAGNÉTICO	
			WEIGHT (g)	%	PESO (g)	%
BM-1	0.5 – 2.0	152.8	14.1	9.2	138.7	90.8
BM-2	0.1 – 0.5	53.8	20.0	37.2	33.8	62.8

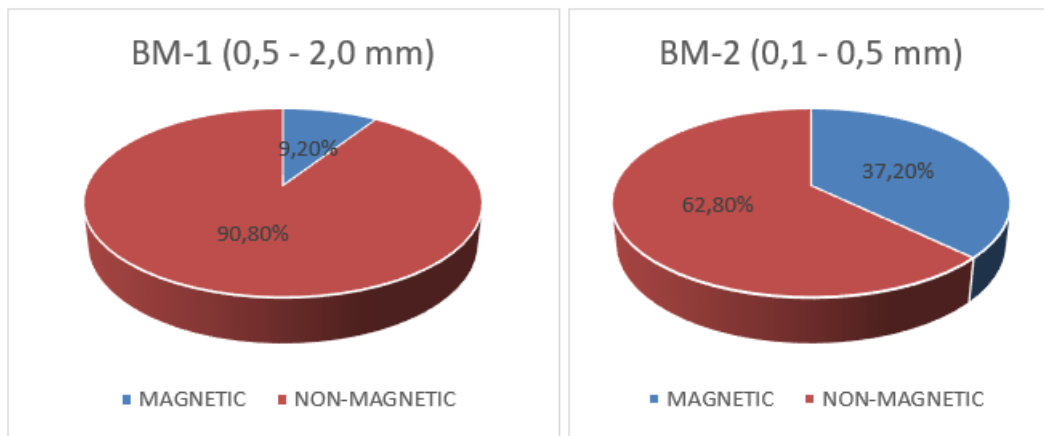


Figure 8-4. Different fractions resulting from the magnetic separator of the El Batán sample.

9. Analysis of the samples separated by the magnetic separator

This section presents the results of the analysis of the samples from La Matona and El Batán carried out in an accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and another percentage analysis of other elements and their oxides (%) called ME_XRF30, from the documentation provided by the laboratory, had been requested. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

Table 9-1 shows the results of the quantitative analyses in parts per million (ppm) obtained from the samples sieved at a particle size of 0.5 - 2.0 mm from La Matona and El Batán. These data can be seen graphically in Figure 9-1. Analysing the result shows a better concentration of the light rare earth elements which remain below 25 ppm except for Itrium (Y), Lanthanum (La), Cerium (Ce) and Neodymium (Nd) which are better concentrated reaching values between 26.50 and 81.30 ppm, in the La Matona sample and Scandium (Sc), Lanthanum (La), Cerium (Ce) and Neodymium (Nd) with values between 30.00 and 70.90 ppm in the El Batán sample. No significant concentration variations between samples are evident.

Table 9-1. Results of the quantitative analysis (ppm) of elements of the samples obtained by the magnetic separator with a particle size of 0.5-2.0 mm.

METHOD	ELEMENT	SAMPLES (ppm)			
		MATONA		BATAN	
		MM-MAG-1	MM-NO.MAG-1	BM-MAG-1	BM-NO.MAG-1
ME-MS89L	Sc	20.00	20.00	20.00	30.00
ME-MS89L	Y	29.90	26.50	22.30	19.60
ME-MS89L	La	36.00	39.00	33.80	30.10
ME-MS89L	Ce	77.30	81.30	70.90	65.70
ME-MS89L	Pr	8.71	10.30	9.38	8.04
ME-MS89L	Nd	33.90	39.20	34.40	31.30
ME-MS89L	Sm	6.77	6.27	5.93	5.47
ME-MS89L	Eu	5.75	1.33	1.29	1.15
ME-MS89L	Gd	5.75	7.59	5.21	4.78
ME-MS89L	Tb	0.99	0.94	0.90	0.70
ME-MS89L	Dy	5.53	4.78	4.31	3.72
ME-MS89L	Ho	1.09	0.92	0.82	0.68
ME-MS89L	Er	3.09	2.61	2.13	2.00
ME-MS89L	Tm	0.44	0.35	0.30	0.25
ME-MS89L	Yb	2.91	2.33	2.31	1.72
ME-MS89L	Lu	0.42	0.37	0.29	0.25
TOTAL		234.23	243.79	214.27	205.46

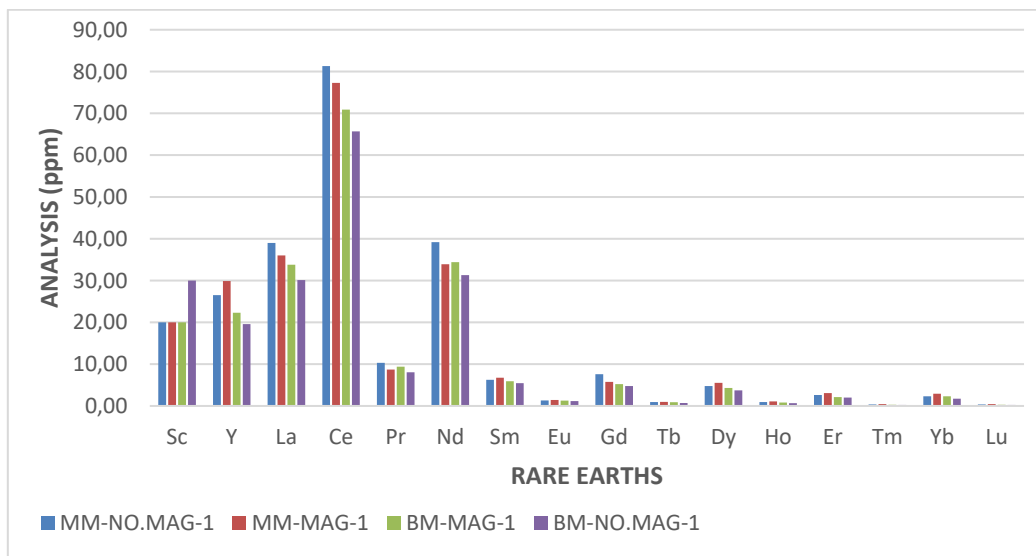


Figure 9-1. Graph of the quantitative analysis of the samples using the magnetic separator with a particle size of 0.5-2.0 mm.

The results of the percentage analysis obtained from the samples obtained from the magnetic separator at La Matona and El Batán with a particle size of 0.5-2.0 mm are shown in Table 9-2 and Figure 9-2. All compounds have a concentration below the detection limit.

Table 9-2. Results of the percentage analysis (%) of the samples from the magnetic separator

METHOD	ELEMENT	SAMPLES (%)			
		MATONA		BM-MAG-1	BM-NO.MAG-1
		MM-MAG-1	MM-NO.MAG-1		
ME-XRF30	La ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	CeO ₂	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01

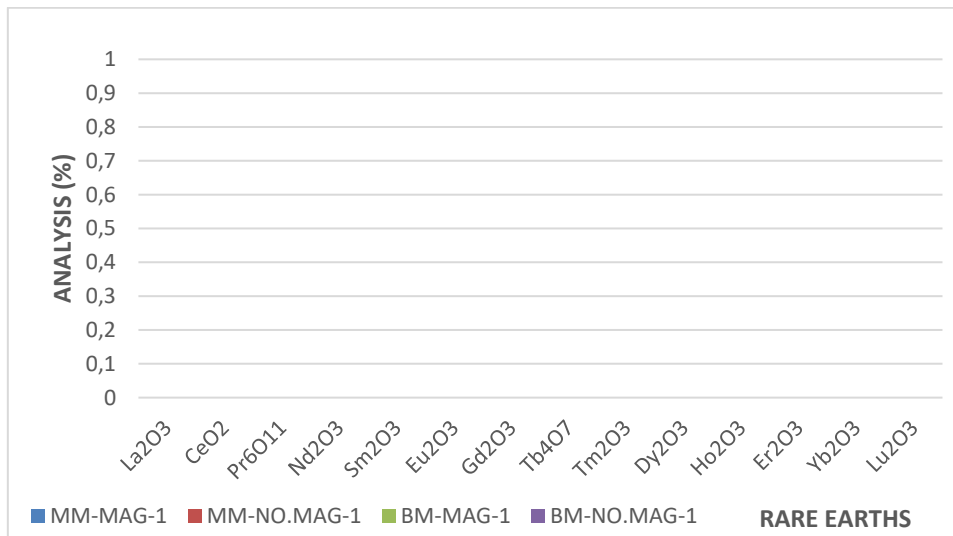


Figure 9-2. Graph of the percentage analysis of the 0.5-2.0 mm samples obtained by the magnetic separator

Table 9-3 presents the quantitative analysis results in parts per million (ppm) obtained from the sieved samples at a grain size of 0.1 - 0.5 mm from La Matona and El Batán. These data can be seen graphically in Figure 9-3 and Figure 9-4, showing that the concentration of the light rare earth elements (LREE) is much better than those of the medium and heavy ones.

Table 9-3. Results of the quantitative analysis (ppm) of elements of the samples obtained by the magnetic separator with a particle size of 0.1-0.5 mm.

METHOD	ELEMENT	SAMPLES (ppm)			
		MATONA		BATAN	
		MM-NO.MAG-2	MM-MAG-2	BM-NO.MAG-2	BM-MAG-2
ME-MS89L	Sc	20.00	30.00	20.00	20.00
ME-MS89L	Y	16.80	26.60	17.90	24.00
ME-MS89L	La	26.80	40.90	24.20	38.50
ME-MS89L	Ce	52.30	81.90	51.40	82.20
ME-MS89L	Pr	6.36	9.83	5.89	8.92
ME-MS89L	Nd	24.20	37.30	21.70	34.80
ME-MS89L	Sm	4.10	7.26	4.50	6.44
ME-MS89L	Eu	0.89	1.48	1.02	1.40
ME-MS89L	Gd	3.86	6.11	3.70	5.28
ME-MS89L	Tb	0.56	0.88	0.59	0.76
ME-MS89L	Dy	2.81	4.55	3.37	4.57
ME-MS89L	Ho	0.61	0.92	0.63	0.80
ME-MS89L	Er	1.91	2.93	1.69	2.45
ME-MS89L	Tm	0.25	0.39	0.24	0.36
ME-MS89L	Yb	1.64	2.49	1.64	2.16
ME-MS89L	Lu	0.25	0.42	0.24	0.37
TOTAL		163.34	253.96	158.71	233.01

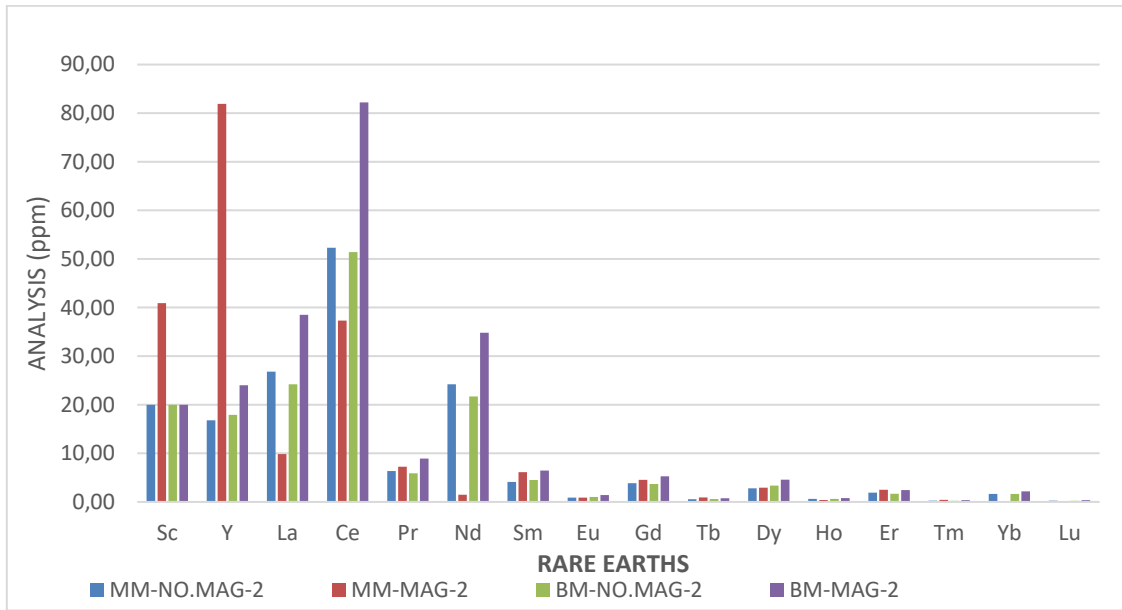


Figure 9-3. Graph of the quantitative analysis of the samples from La Matona using the magnetic separator with a particle size of 0.1-0.5 mm.

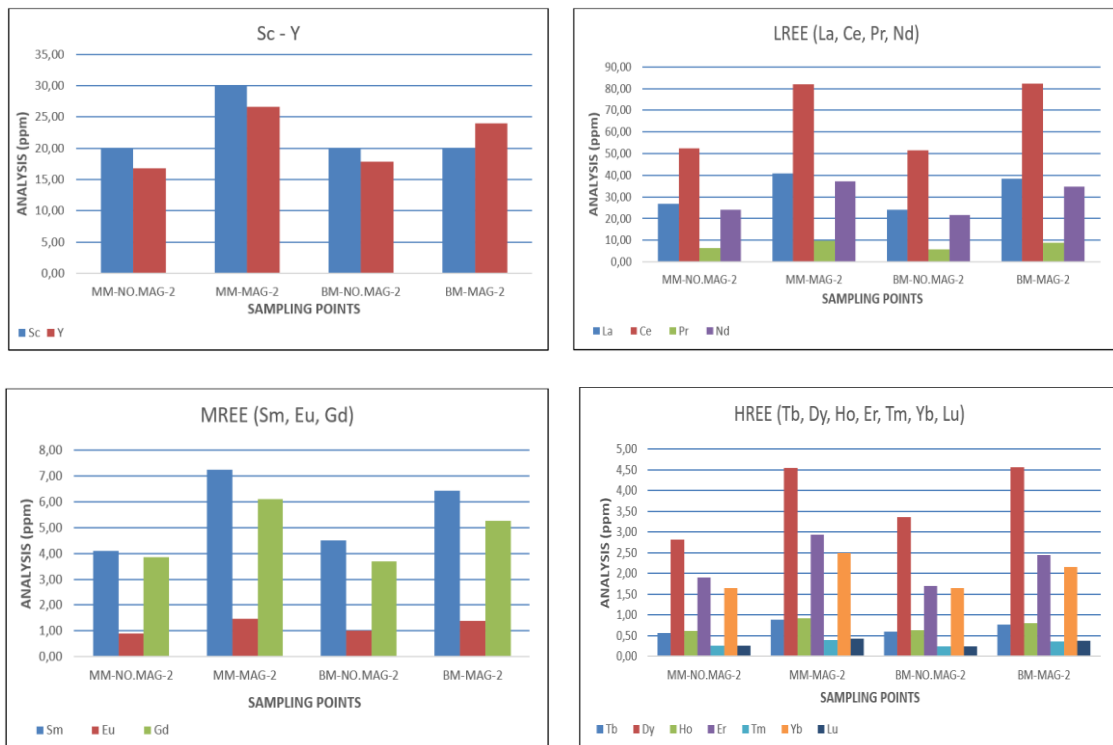


Figure 9-4. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the magnetic separator

There are no significant variations in Scandium (Sc) and Yttrium (Y) concentration. The Cerium (Ce) concentration of the LREE group increases considerably in the magnetic subsamples of both the El Batán and La Matona samples, as do Lanthanum (La) and Neodymium (Nd), whose increases are more moderate. In the MREE group, Samarium (Sm) and Gadolinium (Gd) are more concentrated in the magnetic subgroups of both sampling points. The same happens in the HREE group with Dysprosium (Dy), Erbium (Er) and Ytterbium (Yb).

The results of the percentage analysis obtained from the samples obtained from the magnetic separator at La Matona and El Batán with a particle size of 0.1-0.5 mm are shown in Table 9-4 and in Figure 9-5. It can be seen that the results are below the detection limit except for Cerium Oxide (CeO₂) which reaches a value of 0.01% in the samples from the magnetic separator at La Matona and El Batán.

Table 9-4. Results of the percentage analysis of the samples obtained using the magnetic separator with a particle size of 0.1-0.5 mm

METHOD	ELEMENT	SAMPLES (%)			
		MATONA		BATAN	
		MM-MAG-2	MM-NO.MAG-2	BM-MAG-2	BM-NO.MAG-2
ME-XRF30	La ₂ O ₃	<0.01	<0.01	0.01	<0.01
ME-XRF30	CeO ₂	0.01	0.01	0.01	0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01

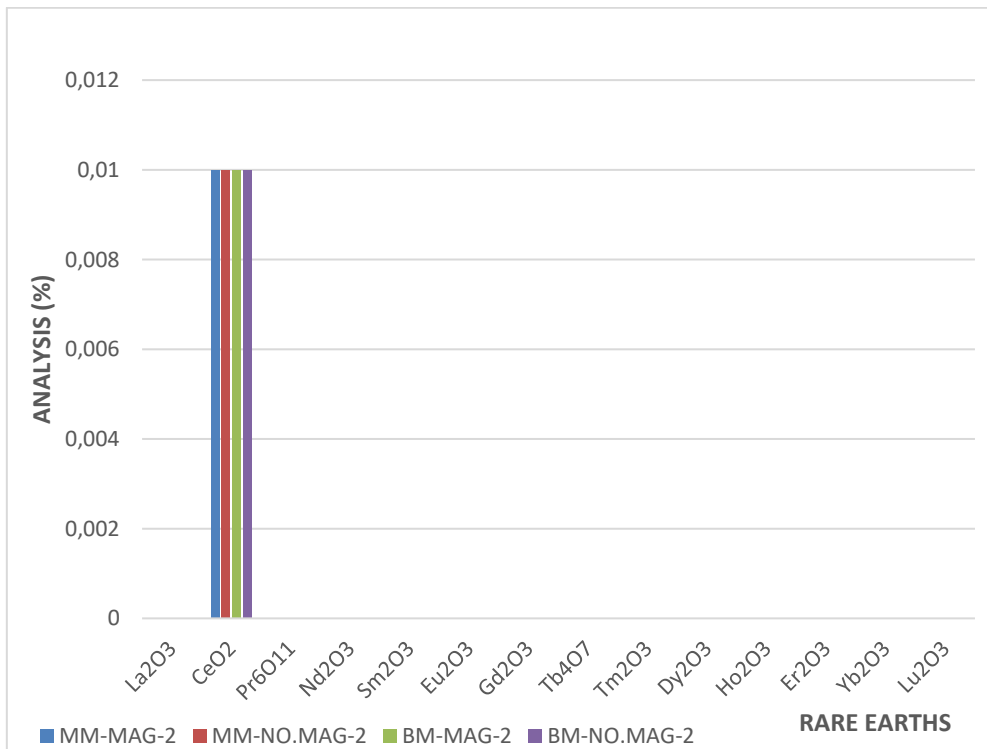


Figure 9-5. Graph of the percentage analysis of the 0.1-0.5 mm samples obtained by the magnetic separator

10. Electric field separation test

Based on the non-conductive character of most rare earth minerals, a high voltage electric field separation (30-40 kV) will be carried out for particle sizes between 0.1 and 0.5 mm (dry route).

This method will take advantage of the difference in the electrical conductivity or surface electrical charge of the mineral species. In this sense, when mineral particles are subjected to the influence of an electric field, depending on their degree of conductivity, they will accumulate a charge whose quantity depends on the maximum accumulable charge density that the particles can reach according to their nature and their surface area. Once the mineral particles have acquired a surface electric charge, they can be separated by differential electrostatic attraction or repulsion.

The electric separator for optimum operation allows the use of material with a particle size of 2.0-0.5 mm.

If a particle is placed on a grounded conductor in the presence of an electric field, the particle will rapidly develop a surface charge by induction. Both a conductive and a dielectric particle will acquire a surface polarisation. However, conductive particles will become surface equipotential (acquiring the polarity and potential of the drum) almost instantaneously through their contact with it (Figure 10-1 a). Whereas a non-conducting particle on the far side of the drum will need more time to acquire the same polarity and potential. Therefore, this type of dielectric particle will remain polarised (Figure 10-1 b).

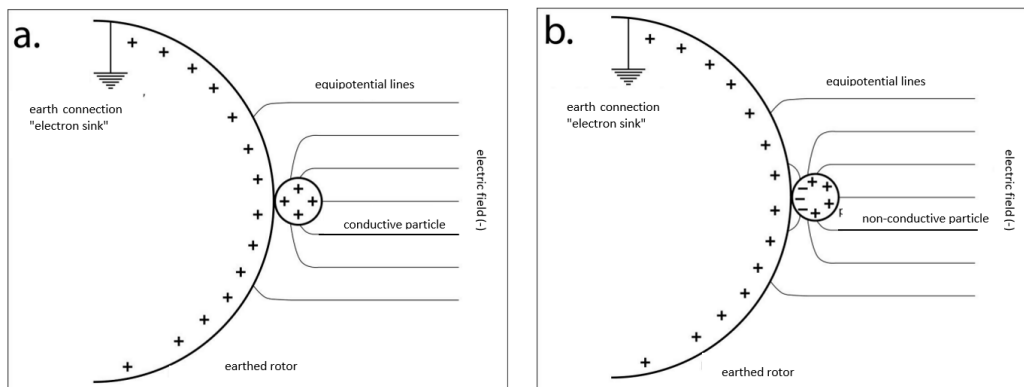


Figure 10-1. Electrification by conductive induction of a conductive particle (a) and a dielectric particle (b).

It can be defined in practical terms that the conductive particles (C) will, in a very short time, assume the potential of the drum, which is opposite to that of the active electrode, and will therefore be attracted to it (Figure 10-2). The non-conductive (NC) particles will be polarised and thus tend, in relation to their polar orientation, to be attached to the

drum and repelled by the electrode. A properly placed separator or cutter can turn these differences in trajectories into an advantage for carrying out mineral separation.

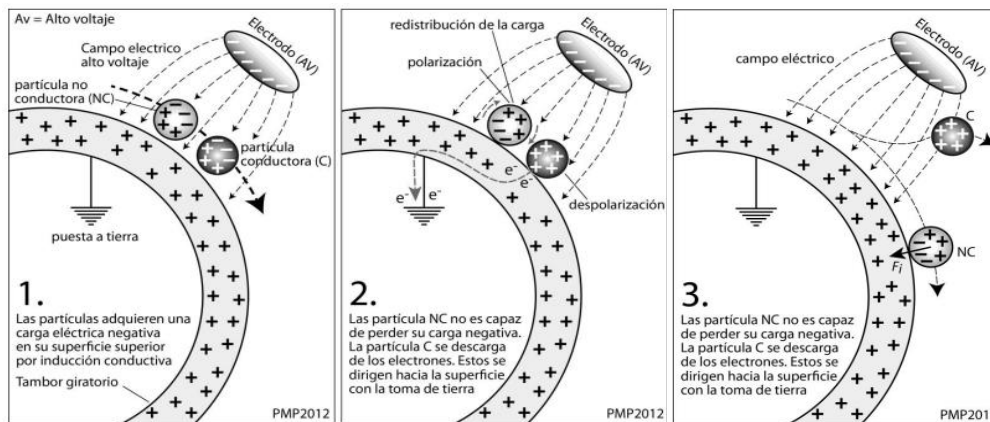


Figure 10-2. Principle of operation of the phenomenon of conduction charging on mineral particles.

10.1. Procedure for electrical separation of samples

This section shall describe the procedure for the electrical separation of samples for analysis in an accredited laboratory. Three samples shall be taken from each raw sample, one consisting of conductive minerals, one of mixed minerals and one of non-conductive minerals.

Dry material sieved to a particle size of 0.5 - 0.1 mm, which has been prepared previously, is taken. This material is introduced into the upper cone of the separator, sliding along the cylinder and interacting with the electric fields. It can be observed how the separation of the material takes place according to its electrical conductivity, which falls into the three lower trays.

Initially, the machine to be used must be cleaned in order to remove any impurities that may exist from previous procedures that could contaminate the samples. Once plugged into the mains, the following variables are entered into the machine:

- Roller speed at 100 r.p.m.
- Infrared lamp on.
- High voltage switched on at 30000 V.

The machines used are as follows:

- Electric separator (Figure 10-3).
- Scales.



Figure 10-3. Electrical separator

10.2. Sample from La Matona (Spain)

55.9 g of material from La Matona with a grain size between 0.1 and 0.5 mm were used. After passing the material through the electric field separator, the different fractions shown in Table 10-1 were obtained.

Table 10-1. Electrical separation of La Matona sample

SAMPLE	GRAIN SIZE (mm)	SAMPLE WEIGHT (mm)	SEPARATION (g)					
			CONDUCTIVE		MIXED		NON-CONDUCTIVE	
			WEIGHT (g)	%	WEIGHT (g)	%	WEIGHT (g)	%
ME-1	0.1 – 0.5	55.9	14.7	26.3	26.1	46.7	15.1	27.0

It is observed that the composition of the sample shows 26.3% of materials with conductors, 27.0% of non-conducting materials and 46.7% of mixed materials (Figure 10-4).

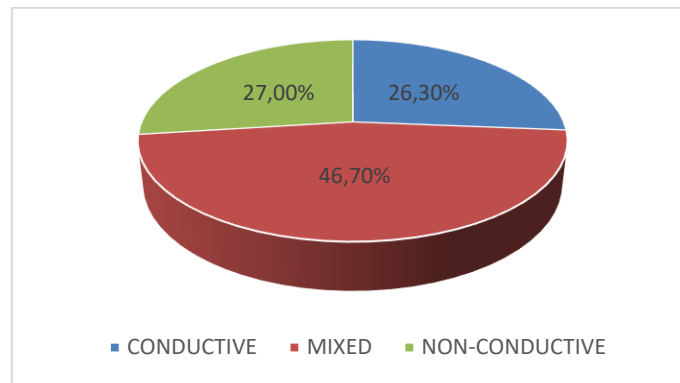


Figure 10-4. Different fractions resulting from the electrical separator of the La Matona sample

10.3. Sample from El Batán (Spain)

71.5 g of material from El Batán with a grain size between 0.1 and 0.5 mm were used. After passing the material through the electric field separator, the different fractions shown in Table 10-2 were obtained.

Table 10-2. Electrical separation of the El Batán sample

SAMPLE	GRAIN SIZE (mm)	SAMPLE WEIGHT (mm)	SEPARATION (g)					
			CONDUCTIVE		MIXTO		NON-CONDUCTIVE	
			WEIGHT (g)	%	WEIGHT (g)	%	WEIGHT (g)	%
BE-1	0.1 – 0.5	71.5	10.3	14.4	30.1	42.1	31.1	43.5

It can be seen that the sample composition shows 14.4% of materials with conductors, 43.5% of non-conducting materials and 42.1% of mixed materials (Figure 10-5).

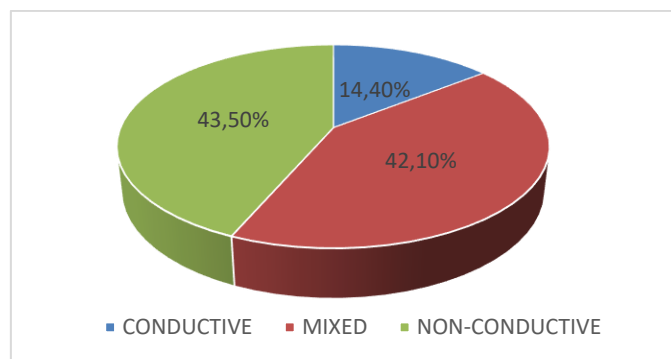


Figure 10-5. Different fractions resulting from the electrical separator of the El Batán sample

11. Analysis of the samples separated by the electrical separator

This section presents the results of the analysis of the samples from La Matona and El Batán carried out in an accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and another percentage analysis of other elements and their oxides (%) called ME_XRF30, from the documentation provided by the laboratory, had been requested. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

Table 11-1 shows the results of the quantitative analyses in parts per million (ppm) obtained from the samples sieved at a particle size of 0.1 - 0.5 mm from La Matona and El Batán. These data can be seen graphically in Figure 11-1 and Figure 11-2. Analysing the result shows a better concentration of the light rare earth elements which remain below 25 ppm except for Lanthanum (La), Cerium (Ce) and Neodymium (Nd) which are better concentrated reaching values between 31.40 and 97.00 ppm.

Table 11-1. Results of the quantitative analysis (ppm) of elements in the samples obtained by the electrical separator.

METHOD	ELEMENT	SAMPLES (ppm)					
		MATONA			BATAN		
		ME-COND	ME-MIXED	ME-NON.COND	BE-COND	BE-MIXED	BE-NON.COND
ME-MS89L	Sc	30.00	20.00	10.00	30.00	20.00	20.00
ME-MS89L	Y	29.70	27.00	24.10	28.70	21.50	18.70
ME-MS89L	La	43.30	38.70	31.40	47.00	38.80	21.90
ME-MS89L	Ce	91.20	80.30	66.50	97.00	76.20	47.00
ME-MS89L	Pr	11.45	10.05	8.38	11.65	8.61	5.78
ME-MS89L	Nd	43.90	38.60	31.80	46.60	34.00	24.10
ME-MS89L	Sm	8.14	6.42	5.52	7.22	6.40	4.32
ME-MS89L	Eu	1.63	1.41	1.05	1.75	1.17	0.95
ME-MS89L	Gd	6.40	5.65	4.78	6.06	5.17	4.24
ME-MS89L	Tb	1.11	0.85	0.74	0.99	0.81	0.67
ME-MS89L	Dy	5.72	4.99	4.08	5.20	3.81	3.68
ME-MS89L	Ho	1.03	0.96	0.79	1.00	0.83	0.67
ME-MS89L	Er	2.99	2.52	2.25	2.90	2.30	1.86
ME-MS89L	Tm	0.47	0.41	0.33	0.46	0.35	0.22
ME-MS89L	Yb	2.60	2.34	2.24	2.71	2.14	1.56
ME-MS89L	Lu	0.37	0.36	0.30	0.36	0.32	0.23
TOTAL		280.01	240.56	194.26	289.60	220.41	155.88

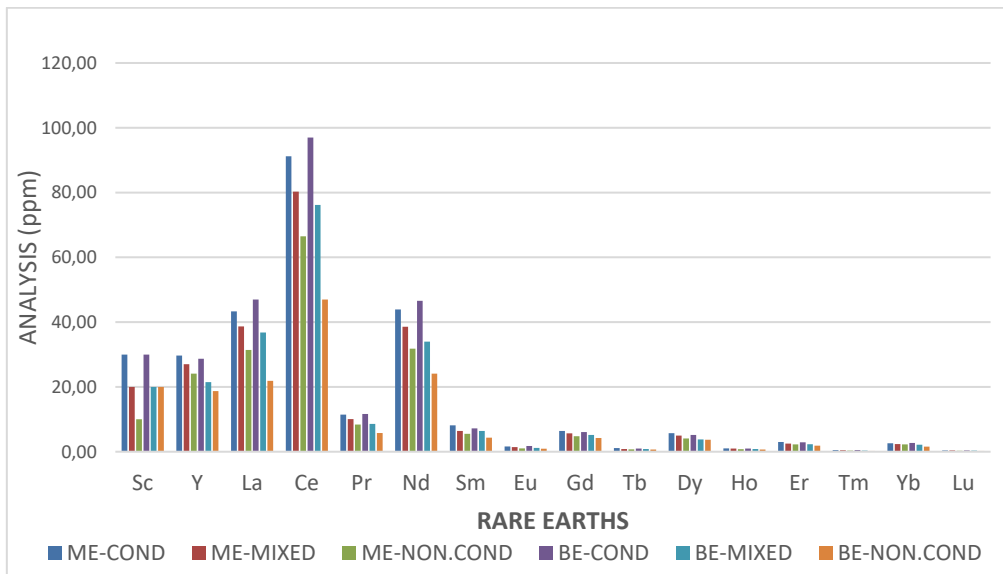


Figure 11-1. Graph of the quantitative analysis of the samples by means of the electrical separator

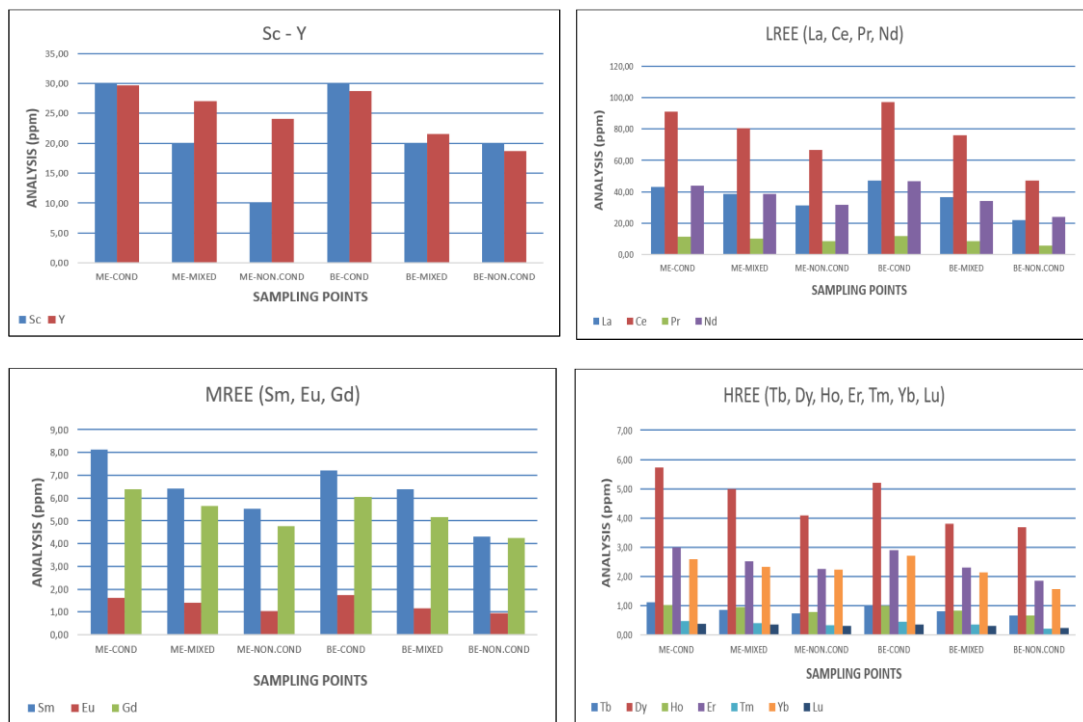


Figure 11-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the electrical separator

A better concentration of both Scandium (Sc) and Yttrium (Y) is observed in both the La Matona and El Batán conductive subgroups, although this can be generalised to all subgroups. In the LREE group, Cerium (Ce) stands out against the other elements, in the

MREE group Samarium (Sm) and Gadolinium (Gd) are much more abundant than Europium (Eu) and in the HREE group Dysprosium (Dy) stands out. In general, there is not much variability in concentrations using this method.

The results of the percentage analysis obtained from the samples obtained from the electrical separator of La Matona and El Batán with a particle size of 0.1-0.5 mm are shown in Table 11-2 and Figure 11-3. It can be seen that the results are below the detection limit except for Lanthanum Oxide (La₂O₃) and Cerium Oxide (CeO₂) which reach a value of 0.01%.

Table 11-2. Results of the percentage analysis (%) of the samples from the electrical separator

METHOD	ELEMENT	SAMPLES (%)					
		MATONA			BATAN		
		ME-COND	ME-MIXED	ME-NON.COND	BE-COND	BE-MIXED	BE-NON.COND
ME-XRF30	La ₂ O ₃	<0.01	0.01	<0.01	<0.01	0.01	0.01
ME-XRF30	CeO ₂	0.01	0.01	<0.01	0.01	0.01	<0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

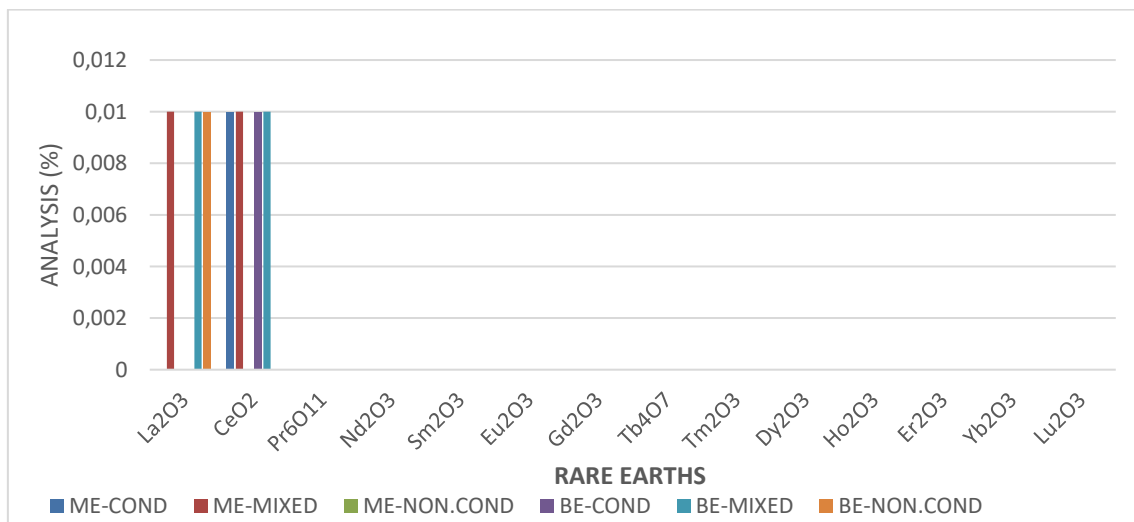


Figure 11-3. Graph of the percentage of analysis of the samples obtained by the electrical separator

12. Shaking table separation test

Since almost all rare earth minerals are very dense, gravimetric concentration analysis will be developed in the first place to obtain a dense wet concentrate. The equipment to be used will depend on the liberation analysis: multigravity separator for sizes <0.1 mm, shaking tables for sizes between 0.1 and 0.5 mm, and pulsation box for sizes between 0.5 and 2.0 mm. We will analyse here the shaking table separation test.

The shaking table is a flat table top with a vibrating forward and backward motion used to separate fine and heavy particles from coarse and light particles.

The table is subjected to two movements, a very fast backward movement and a very slow forward movement. In this way, together with the slow movement, the pulp is transported to the end of the table. As the pulp moves forward, the riffles or ridges decrease in height and this causes the cross flow of water to remove the light, stratified particles from the top of the table and to move the heavy particles towards the end of the table.

The mineral is distributed on the table in a fan shape due to the different slow forward and fast backward movement and the cross flow of the water and the particles are able to be layered behind the table shoulders. The flow of the water sheet systematically separates the lighter particles in the upper stratified layers from the heavier ones (Figure 12-1).

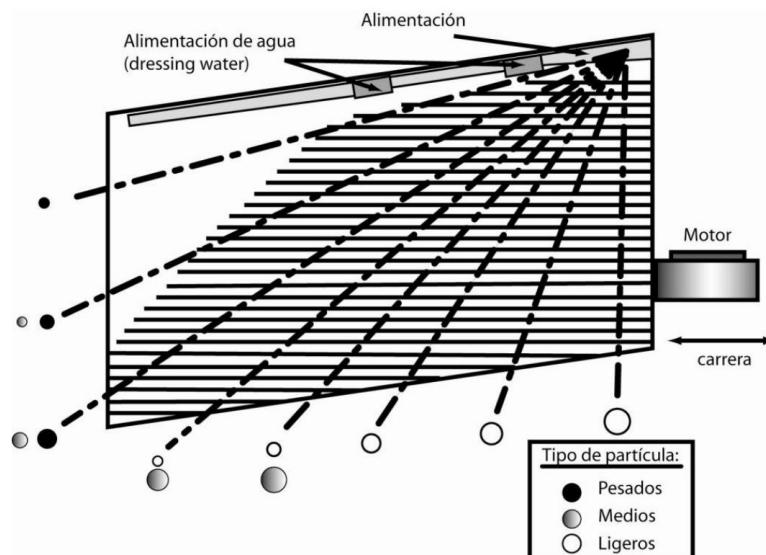


Figure 12-1. Particle distribution on a shaking table

The water used in the process is made up of the water attached to the feed pulp and the water supplied to the table (dressing water). The feed consisting of the tailings mixed

with water is carried out at the top of the shaking table. The particle layer reaching the end zone of the shaking table will be composed of only one or two ore particles.

According to Bird & Davis (1929), only a part of the water flow will circulate through the top of the ore layer while the rest will circulate through the interstices created between the particles. The interstices between the particles are larger in the upper part of the mineral layer than in the lower part of the mineral layer, so that the flows are faster at the top than at the bottom. This results in a sorting of the particulate material by particle size in the different layers. These streams will carry the light fine particles at a higher velocity between the shoulders than the heavy particles of the same diameter.

The material particles undergo the following phenomena when they are on the shaking table:

- Stratification: Coarse particles with equal density are deposited on top and small particles on the bottom. This process is easy for small and heavy particles while it is difficult due to hindered sedimentation by table protrusions.
- Hindered sedimentation: Coarse particles with equal density are deposited at the bottom and small particles at the top. This process results in easy separation of the large heavy particles due to the obstacles but is difficult due to stratification.

The factors that need to be monitored for optimal concentration on the shaking table are:

- Horizontal vibratory motion:
 - Slow forward and fast reverse.
 - 250-300 strokes per minute.
 - 10 – 25 mm stroke length.
- Water flow: 75 % feed water and 25 % dressing water.
- Table slope:
 - ♣ Table is slightly inclined towards the reject zone (ore concentrate).
 - ♣ the table is slightly elevated along the line of movement from the feed end to the concentrate end.
- Riffles:
 - ♣ Their height and spacing are important variables.
 - ♣ They hinder the advance of heavy particles.

Tables for table concentrates are used in the processing of tin, iron, tungsten, tantalum, mica, barium, titanium, zirconium, gold, silver, uranium, etc. ores. However, their main use is in the washing of coals.

12.1. Procedure for shaking table separation of the samples

In this section, the procedure for gravimetric separation of samples for analysis in an accredited laboratory will be described. A quantity of material with a grain size between 0.1 and 0.5 mm was prepared. The machines used are as follows:

- Shaking table (Figure 12-2).
- Stove.
- Scale.



Figure 12-2. Shaking table

The table must be cleaned initially to avoid possible contamination due to previous processes. Containers are placed in the different areas (Figure 12-3) of the machine to collect the different types of material to be deposited (light, mixed and dense). It is necessary to check that all the water that will carry the sample is collected and that no fraction of material is lost.



Figure 12-3. Exit areas of the different fractions of the shaking table

The sample from La Matona requires the sample to be slightly inclined to favour the sliding of the material, while the sample from El Batán will be placed horizontally on the table.

The water in the upper right-hand side is opened and the sample is gradually deposited in the trough, previously mixed with water in a container, until the test is completed, i.e. when there is no sample in the container and the table is clean and contains no material.

12.2. Sample from La Matona (Spain)

A 1 kg sample with a grain size between 0.1 and 0.5 mm was prepared from material from La Matona. This material was washed on a 0.1 mm sieve to ensure that no undersize fractions are present. The total sample that was passed through the shaking table was 559.0 g, from which the different fractions (Dense, Light and Mixed) are obtained after the test, as shown in Table 12-1 and visually analysed in Figure 12-4.

Table 12-1. Gravimetric shaking table separation of the La Matona sample

SAMPLE	NAME	WEIGHT (g)
MS-DENSE	MS-D	390.6
MS-LIGHT	MS-L	32.3
MS-MIXED	MS-MIX	136.1
TOTAL		559.0

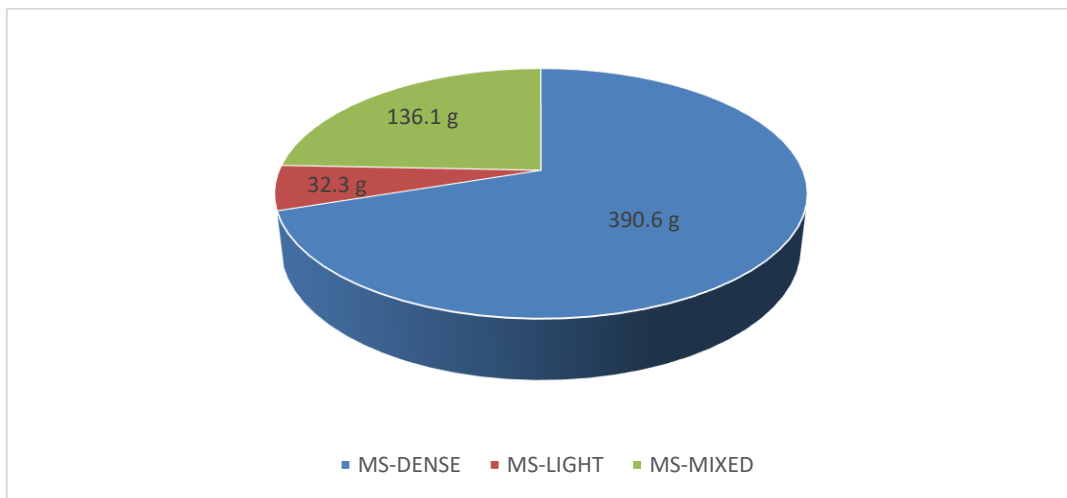


Figure 12-4. Graph of the shaking table separation of the La Matona sample.

12.3. Sample from El Batán (Spain)

A sample of 1.2 kg of material from El Batán with a grain size between 0.1 and 0.5 mm was prepared. This material was washed on a 0.1 mm sieve to ensure that no undersize fractions are present. The total sample that was passed through the shaking table was

364.7 g, from which the different fractions (Dense, Light and Mixed) are obtained after the test, as shown in Table 12-2 and analysed visually in Figure 12-5.

Table 12-2. Gravimetric shaking table separation of the El Batán sample

SAMPLE	NAME	WEIGHT (g)
BS-DENSE	BS-D	189.2
BS-LIGHT	BS-L	142.5
BS-MIXED	BS-MIX	33.0
TOTALES		364.7

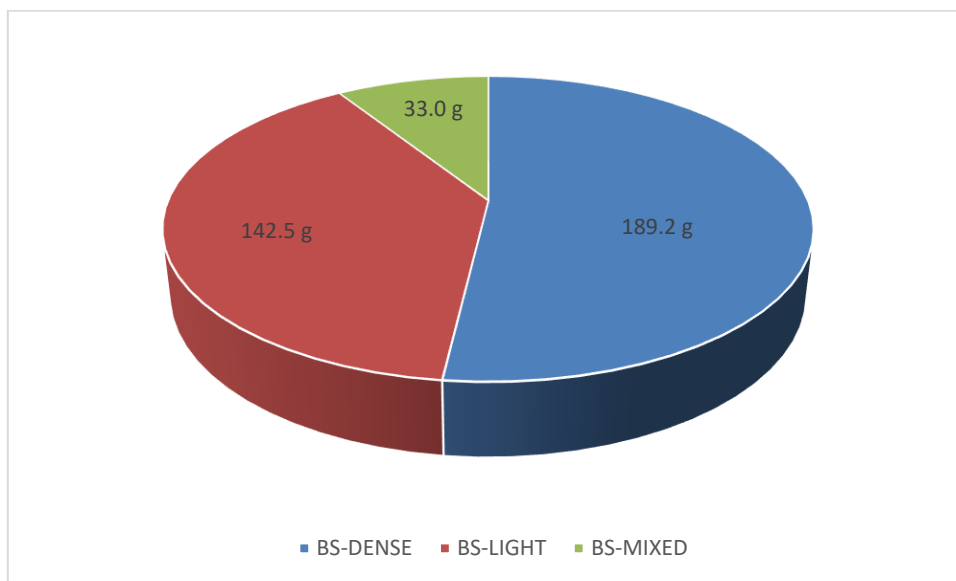


Figure 12-5. Graph of the shaking table separation of the El Batán sample by sector.

13. Analysis of the samples separated by the shaking table

This section presents the results of the analysis of the samples from La Matona and El Batán carried out in an accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and another percentage analysis of other elements and their oxides (%) called ME_XRF30, from the documentation provided by the laboratory, had been requested. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

Table 13-1 shows the results of the quantitative analyses in parts per million (ppm) obtained from the samples sieved at a particle size of 0.1 - 0.5 mm from La Matona and El Batán. These data can be seen graphically in Figure 13-1 and Figure 13-2. Analysing the result shows a better concentration of the light rare earth elements which remain below 25 ppm except for the Dense subsample of Scandium (Sc) and Itrium (Y) from El Batán sample which exceed 30 ppm and Lanthanum (La), Cerium (Ce) and Neodymium (Nd) which are better concentrated reaching values between 30.30 and 108.50 ppm.

Table 13-1. Results of the quantitative analysis (ppm) of elements of the samples obtained by the shaking table

METHOD	ELEMENT	SAMPLES (ppm)					
		MATONA			BATAN		
		MS-DENSE	MS-LIGHT	MS-MIXED	BS-DENSE	BS-LIGHT	BS-MIXED
ME-MS89L	Sc	20.00	10.00	20.00	30.00	20.00	20.00
ME-MS89L	Y	20.80	23.20	22.90	28.60	19.40	14.70
ME-MS89L	La	31.50	20.70	30.70	53.80	27.10	21.30
ME-MS89L	Ce	63.90	44.90	65.80	108.50	57.40	43.20
ME-MS89L	Pr	8.16	5.58	8.20	11.90	6.33	4.88
ME-MS89L	Nd	30.30	21.90	32.60	43.90	24.00	18.05
ME-MS89L	Sm	5.51	3.63	5.95	8.79	4.65	3.62
ME-MS89L	Eu	1.32	0.78	1.17	1.52	0.88	0.83
ME-MS89L	Gd	4.42	3.79	4.78	6.65	3.88	3.28
ME-MS89L	Tb	0.78	0.69	0.75	0.99	0.62	0.48
ME-MS89L	Dy	3.79	3.61	4.35	5.36	3.56	3.02
ME-MS89L	Ho	0.72	0.70	0.75	1.09	0.69	0.58
ME-MS89L	Er	2.21	2.24	2.24	3.12	2.14	1.68
ME-MS89L	Tm	0.30	0.30	0.30	0.49	0.29	0.22
ME-MS89L	Yb	2.03	2.28	2.14	2.87	1.79	1.39
ME-MS89L	Lu	0.39	0.24	0.28	0.46	0.30	0.24
TOTAL		196.13	144.54	202.91	308.04	173.03	137.47

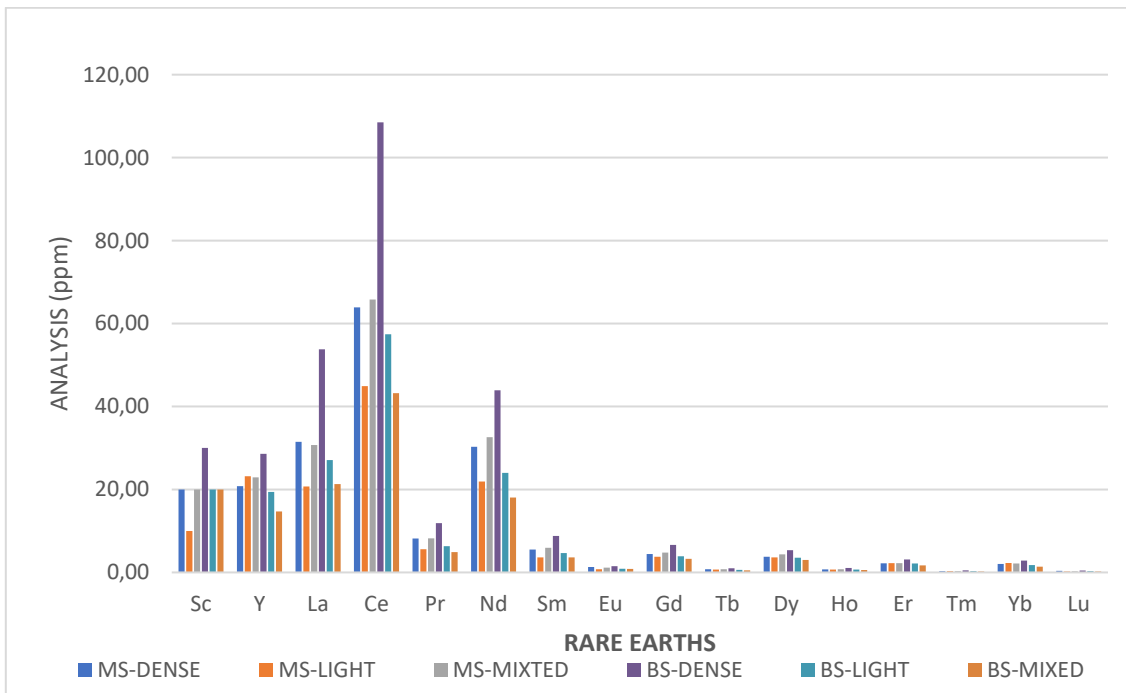


Figure 13-1. Graph of quantitative analysis of the samples using shaking table

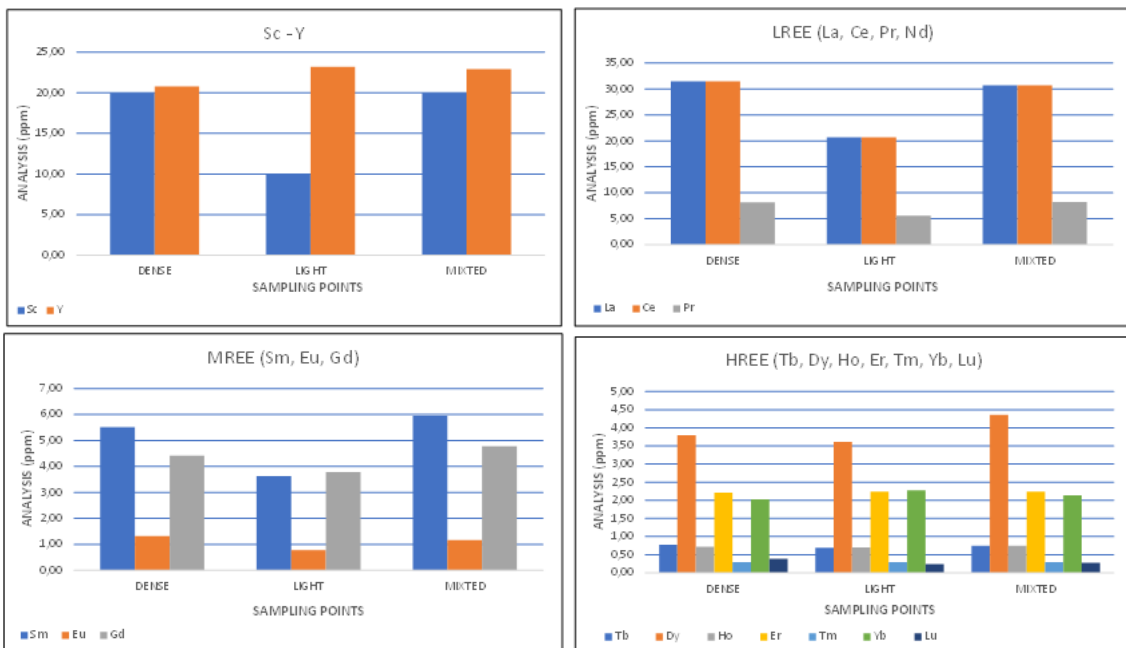


Figure 13-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the shaking table

The results of the percentage analysis obtained from the samples obtained from the shaking table of La Matona and El Batán with a particle size of 0.1-0.5 mm are reflected

in Table 13-2 and Figure 13-3. It is observed that the results are below the detection limit except for Lanthanum Oxide (La₂O₃) and Cerium Oxide (CeO₂) which reach the value of 0.01%.

Table 13-2. Results of the percentage analysis (%) of the shaking table samples

METHOD	ELEMENT	SAMPLES (%)					
		MATONA			BATAN		
		MS-DENSE	MS-LIGHT	MS-MIXED	BS-DENSE	BS-LIGHT	BS-MIXED
ME-XRF30	La ₂ O ₃	<0.01	0.01	<0.01	<0.01	0.01	0.01
ME-XRF30	CeO ₂	0.01	0.01	<0.01	0.01	0.01	<0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

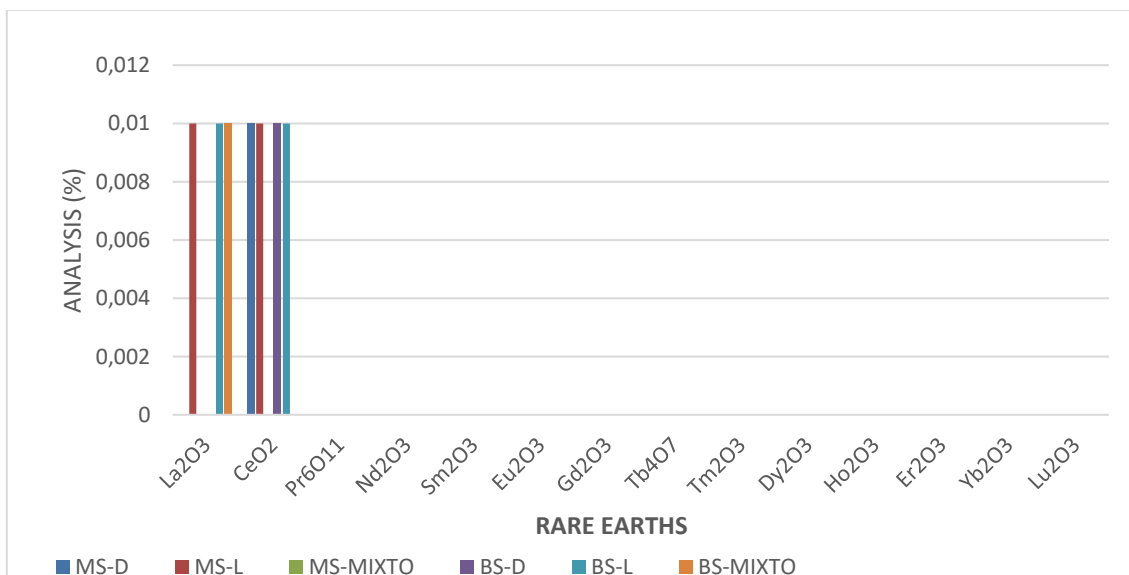


Figure 13-3. Graph of the percentage analysis of the samples obtained using the shaking table.

14. Froth Flotation Test

Based on the non-conductive character of most rare earth minerals, a froth flotation test for particles >0.02 mm will be analysed in this chapter.

Flotation is a phase of mineral concentration that occurs in liquid, solid and gaseous states. The valuable mineral is separated from non-valuable material by taking advantage of its physical-chemical characteristics through the addition of reagents; this leads to the generation of froth and its subsequent collection by flotation cells.

Froth flotation takes place as follows: once the hydrophobic particles are attached to the bubbles (at the boundary of the liquid and gas phases), flotation complexes are formed, which form a foam-product when they emerge on the pulp surface.

This method requires the use of a material with a particle size of <0.1 mm to work optimally.

14.1. Froth flotation procedure of the samples

This section will describe the foam flotation separation procedure of the samples for an analysis in an accredited laboratory. A quantity of material of grain size less than 0.1 mm was prepared.

The machines used are as follows:

- Flotation cell (
-
-

-
- Oven.
- Scale.



Figura

14-1).

Figura 14-1. Flotation cell

The machine must be cleaned initially to avoid possible contamination due to previous processes. A container for mixing and a container for collecting the froth is required.

The procedure for carrying out the foam flotation test is described below:

- The machine is switched on with clean water in the flotation cell for pre-cleaning.
- Weigh 200 g of material with a grain size of less than 0.1 mm.
- Mix the 200 g of material with water in the cell by operating the machine at 1250 rpm of the rotation axis.
- Add 2 drops of cherosene, which is a collector that hydrophobises the mineral phases to be enhanced.
- Leave the machine moving the mixture for 5 minutes.
- Add 2 drops of MiBC, which is a foaming agent that gives stability to the foams.
- Leave the machine moving the mixture for a further 1 minute.
- The air is turned on at the valve at the top of the machine and the process begins. The agitator causes the material particles to impact against the air bubbles and if they are hydrophobic, they adhere to them and form the foams. These foams overflow the cell tank and fall into the tray. Large bubbles should be collected with a spoon to help them slide into the tray. Once the tray is full, the bubbles should be replaced as necessary until the end of the process.
- It is necessary to replace some of the water that is eliminated by the foams, which become smaller and smaller and browner as they are less and less loaded with particles.
- This process is carried out until the final exhaustion, which is when no more foams are produced. The bubbles break and no more foam is generated.
- Two more drops of cherosene are added, leaving the machine agitating for 5 minutes with the air closed. This is done in order to check that no more foams are generated and that the process is finished.
- The foam trays and the flotation cell vessel are placed in the oven at 105°C until completely dry for subsequent analysis of both ash and rare earths.

Finally, two types of samples will be obtained in this test, one with the foam material (Float) and the other with the flotation cell material (Colas).

14.2. Sample from La Matona (Spain)

A 200 g sample of less than 0.1 mm grain size was prepared from material from La Matona. This material was introduced into the flotation cell as described above, obtaining the different fractions of the test (Float and Colas) shown in Table 14-1 and visually analysed in Figure 14-1.

Table 14-1. Foam Flotation Cell Separation of the La Matona Sample

SAMPLE	NAME	WEIGHT (g)
MF-FLOAT	MF-F	12.5
MF-COLAS	MF-C	185.7
TOTAL		198.2

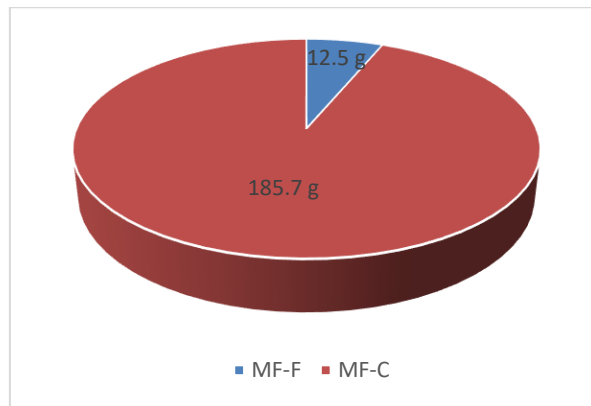


Figure 14-1. Separation graph in the froth flotation cell of the La Matona sample

14.3. Sample from El Batán (Spain)

A 200 g sample with a grain size of less than 0.1 mm was prepared from material from El Batán. This material was introduced into the flotation cell as described above, obtaining the different fractions of the test (Float and Colas) shown in Table 14-2 and visually analysed in Figure 14-2.

Table 14-2. Foam Flotation Cell Separation of El Batán Sample

SAMPLE	NAME	WEIGHT (g)
BF-FLOAT	BF-F	131.3
BF-COLAS	BF-C	66.9
TOTAL		198.2

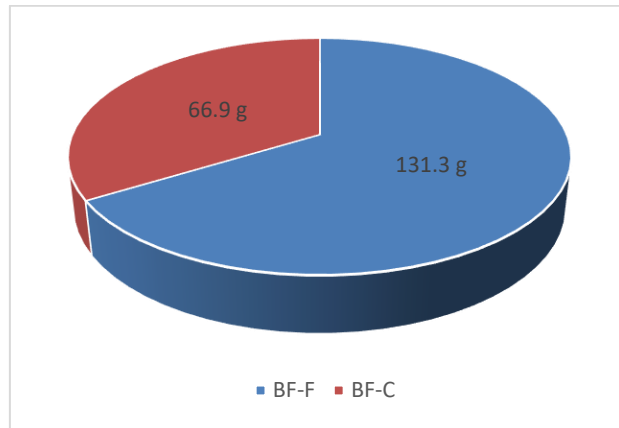


Figure 14-2. Separation graph of El Batán sample in the Froth Flotation Cell.

15. Analysis of samples separated by froth flotation

This section presents the results of the analysis of the samples from La Matona and El Batán carried out in an accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and another percentage analysis of other elements and their oxides (%) called ME_XRF30, from the documentation provided by the laboratory, had been requested. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

Table 15-1 presents the quantitative analysis results in parts per million (ppm) obtained from the samples sieved at a particle size of <0.1 mm from La Matona and El Batán. These data can be seen graphically in Figure 15-1. Analysing the result shows a better concentration of the light rare earth elements (LREE), although in general, there is not much variability in concentrations using this method (Figure 15-2).

Table 15-1. Results of the quantitative analysis (ppm) of elements in the samples obtained by froth flotation

METHOD	ELEMENT	SAMPLES (ppm)			
		MATONA		BATAN	
		MF-FLOATED	MF-COLAS	BF-FLOATED	BF-COLAS
ME-MS89L	Sc	10.00	20.00	10.00	20.00
ME-MS89L	Y	21.20	31.00	17.80	25.90
ME-MS89L	La	25.00	35.20	19.85	45.90
ME-MS89L	Ce	54.30	72.80	41.60	89.70
ME-MS89L	Pr	6.66	9.55	5.08	10.50
ME-MS89L	Nd	26.10	37.70	21.90	39.40
ME-MS89L	Sm	4.60	7.49	3.90	7.63
ME-MS89L	Eu	1.10	1.54	0.96	1.58
ME-MS89L	Gd	4.05	5.79	3.44	6.78
ME-MS89L	Tb	0.66	0.95	0.58	0.94
ME-MS89L	Dy	3.88	5.26	3.48	4.32
ME-MS89L	Ho	0.79	1.02	0.63	0.95
ME-MS89L	Er	2.35	3.14	1.68	2.93
ME-MS89L	Tm	0.24	0.47	0.22	0.41
ME-MS89L	Yb	1.72	2.67	1.66	2.63
ME-MS89L	Lu	0.28	0.44	0.26	0.35
TOTAL		162,93	235,02	133,04	259,92

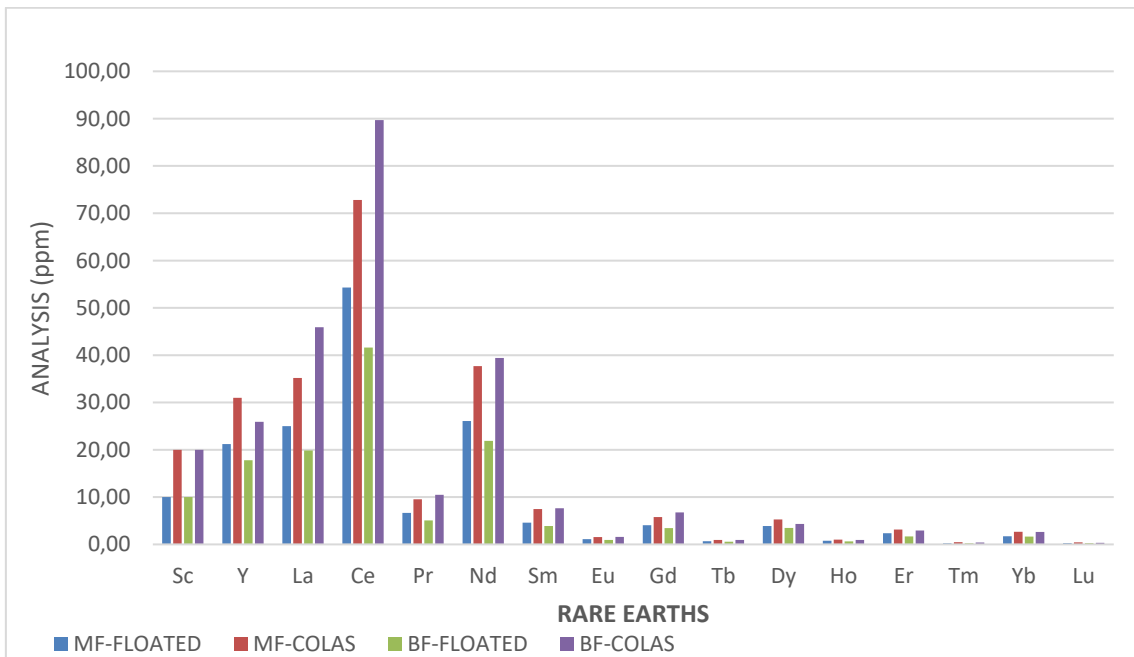


Figure 15-1. Graph of quantitative analysis of samples using froth flotation

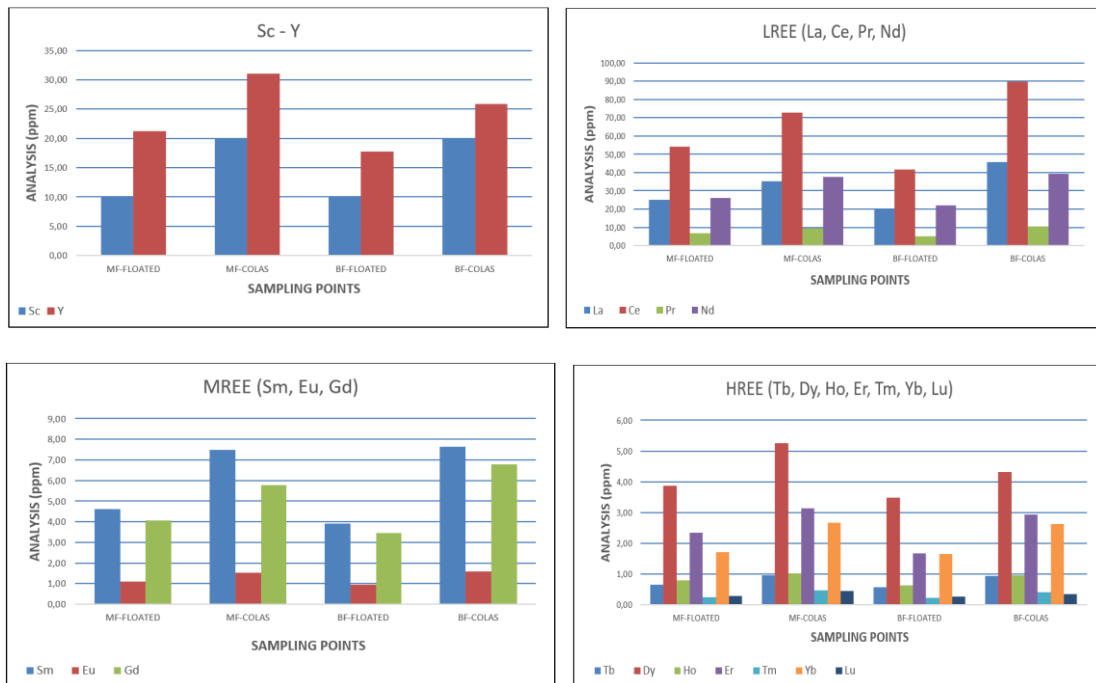


Figure 15-2. Comparisons of the different rare earth groups (Sc-Y, LREE, MREE and HREE) in samples from Spain (La Matona and El Batán) obtained by the froth flotation

The results of the percentage analysis obtained from the samples obtained from the foam flotation of La Matona and El Batán with a particle size <0.1 mm are shown in Table 15-2 and Figure 15-3. It is observed that the results are below the detection limit except for Lanthanum Oxide (La₂O₃), Cerium Oxide (CeO₂) and Neodymium Oxide (Nd₂O₃) which reach a value of 0.01%.

Table 15-2. Results of percentage analysis (%) of froth flotation samples

METHOD	ELEMENT	SAMPLES (%)			
		MATONA		BATAN	
		MS-FLOTADO	MS-COLAS	BS-FLOTADO	BS-COLAS
ME-XRF30	La ₂ O ₃	0.01	<0.01	0.01	0.01
ME-XRF30	CeO ₂	0.01	0.01	<0.01	0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	<0.01	0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01

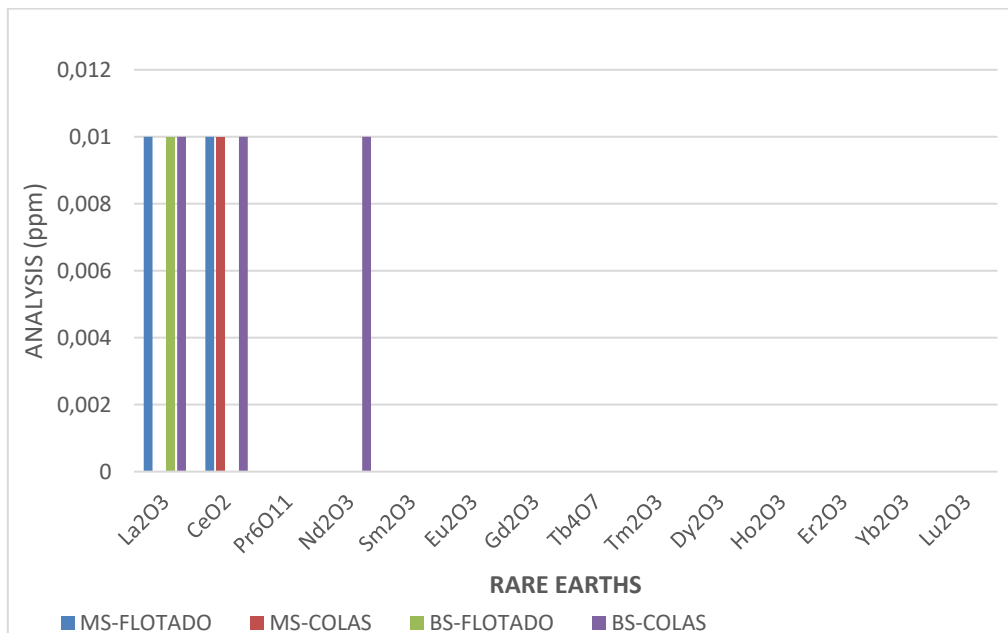


Figure 15-3. Graph of percentage analysis of samples obtained by froth flotation

16. Mozley Multigravimetric Concentration Test (MGS)

Finally, wet gravimetric concentration analysis will be developed with multigravity separator, which is commonly used for sizes <0.1 mm.

The equipment is designed to separate and upgrade finer metals and minerals based on specific gravity difference. The optimum feed comprises materials in the range of 5 to 120 microns. It uses a similar separation principle as a gravity concentration table but improves the degree of separation and capacity several times over by rolling the normally horizontal separating surface of a gravity table into a conical drum. When in rotation it develops a force many times greater than gravity causing the finer particles to separate within the dynamic thin liquid film coating the inner surface of the drum. The rotational speed and degree of shaking can be adjusted to provide a high degree of selectivity in operation, enabling the equipment to achieve the required recovery and grade of concentrate to meet the needs of the intended application. The internal scraper blades convey the heavy concentrate to the front of the drum, while the lighter material is washed to the back of the drum as a tailings stream.

The equipment consists of a slightly open drum at one end and rotates clockwise (viewed from the open side) while being shaken axially in a sinusoidal motion. Inside the drum is a scraper which rotates in the same direction as the drum, but at a slightly faster speed.

The fed pulp is continuously fed from a middle position along the inner surface of the drum via an annular trough. Wash water is added through a trough located near the open side of the drum.

As a result of the high centrifugal forces and the shaking effect, the dense particles migrate through a film of pulp to form a semi-solid layer against the drum wall. Scrapers move the dense layer towards the open end of the drum where the layers discharge into a concentrate chute. The wash water carries the less dense minerals downstream to the back of the drum to discharge them through slots in the tailings chute.

16.1. Multigravimetric concentration procedure for samples

This section will describe the procedure of multigravimetric concentration (MMGS) of the samples for an analysis in an accredited laboratory. A quantity of material with a grain size of less than 0.1 mm was prepared.

Las máquinas utilizadas son las siguientes:

- Mozley Multigravimetric Separator (Figure 16-1).
- Oven.
- Scale.



Figure 16-1. Mozley Multigravimetric Separator

The machine must be cleaned initially to avoid possible contamination due to previous processes. Several large containers are needed to collect all fractions resulting from the test (Dense, Light 1, Light 2 and Washed).

The test procedure is as follows:

- 850 g of material with a grain size of less than 0.1 mm is weighed and mixed with 850 g of water avoiding lumps.
- The multigravimetric separation equipment is switched on at 240 r.p.m. and a wash water flow rate of 3 litres/min.
- The material is fed through the top of the equipment little by little until it is finished. While the equipment is being fed, the output of the "Light 1" material can be observed, and some "Dense" material may be seen.
- Once the feeding of the equipment is finished, the "Light 1" container is changed immediately, and the machine is left running for 3 minutes obtaining "Light 2" and "Dense". After this time, the equipment is switched off.
- Subsequently, the equipment is thoroughly washed, removing the top cover, and all the water with washing material is collected in another container called "Washings".
- The different containers are allowed to sediment and as much water as possible is removed and the material is placed in properly labelled trays which are taken to the oven at 105°C until completely dry.

The material obtained after passing through the oven will be analysed for rare earths. Only rare earths from "Light 1" and "Dense" will be analysed as these fractions are the ones that would only be obtained if the equipment were in continuous operation.

16.2. Sample from La Matona (Spain)

A sample of 850 g of material with a grain size of less than 0.1 mm from La Matona was prepared. This material was introduced into the Mozley Multigravimetric Separator as described above, obtaining the different fractions of the test (Dense, Light 1, Light 2 and Washed) shown in Table 16-1 and analysed visually in Figure 16-2.

Table 16-1. Results of the Mozley Multigravimetric Separation (MGS) of La Matona sample.

SAMPLE	NAME	WEIGHT (g)
MMGS-DENSE	MMGS-D	294.8
MMGS-LIGHT 1	MMGS-L1	329.5
MMGS-LIGHT 2	MMGS-L2	79.3
MMGS-WASHED	MMGS-F	134.6
TOTAL		838.2

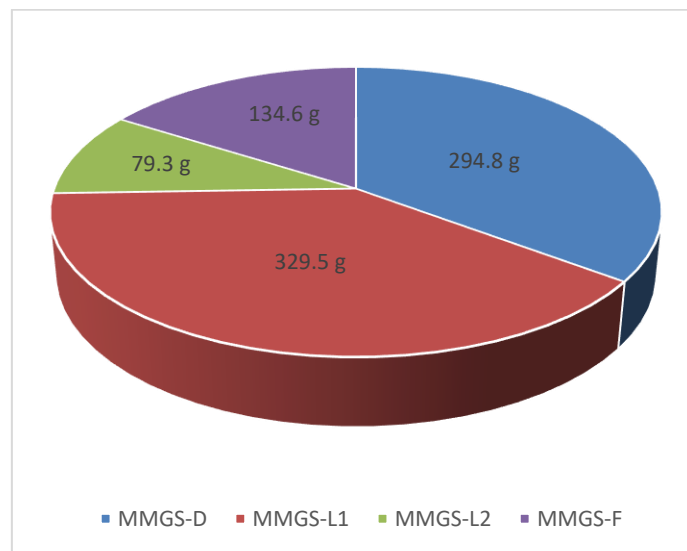


Figure 16-2. Mozley Multigravimetric Separation (MGS) graph of La Matona sample.

16.3. Sample from El Batán (Spain)

A sample of 850 g of material from El Batán with a grain size of less than 0.1 mm was prepared. This material was introduced into the Mozley multigravimetric separator as described above, obtaining the different fractions of the test (Dense, Light 1, Light 2 and Washed) shown in Table 16-2 and analysed visually in Figure 16-3.

Table 16-2. Results of Mozley Multigravimetric Separation (MGS) of El Batán sample.

SAMPLE	MAME	PESO (g)
BMGS-DENSE	BMGS-D	38.8
BMGS-LIGHT 1	BMGS-L1	488,.1
BMGS-LIGHT 2	BMGS-L2	150.6
BMGS-WASHED	BMGS-F	112.0
TOTAL		789.5

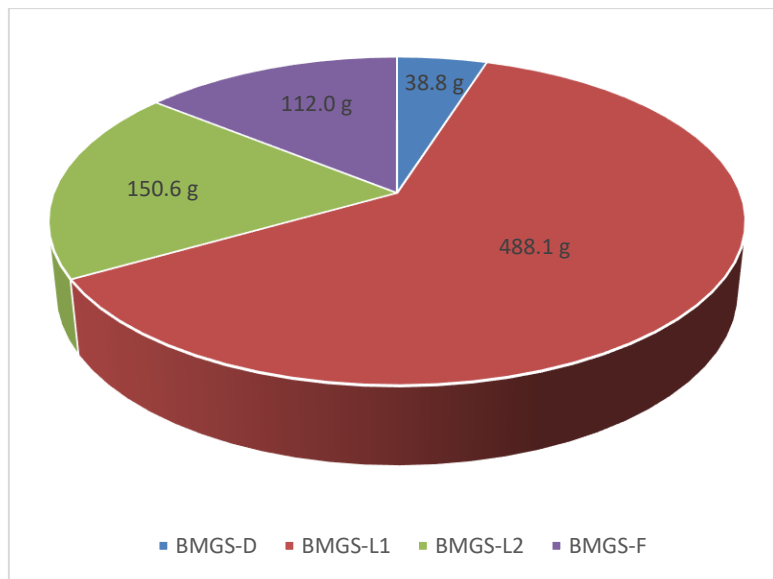


Figure 16-3. Mozley Multigravimetric Separation (MGS) graph of El Batán sample.

17. Analysis of separated samples by Mozley multigravimetric separation (MGS)

This section presents the results of the analysis of the samples from La Matona and El Batán carried out in an accredited laboratory.

A quantitative analysis of some elements (ppm) called ME-MS89L and another percentage analysis of other elements and their oxides (%) called ME_XRF30, from the documentation provided by the laboratory, had been requested. In addition, the elements Hf, Zr and Sc, which were not included in the laboratory tables, were introduced for analysis using the ME-MS89L method. Prior to the analysis, the submitted samples were pulverised to a size of 75 µm.

Table 17-1 presents the quantitative analysis results in parts per million (ppm) obtained from the samples sieved at a particle size of <0.1 mm from La Matona and El Batán. These data can be seen graphically in Figure 17-1. Analysing the result shows a better concentration of the light rare earth elements.

Table 17-1. Results of the quantitative analysis (ppm) of elements in the samples obtained by the Mozley multigravimetric separation.

METHOD	ELEMENT	SAMPLES (ppm)			
		MATONA		BATAN	
		MMGS-DENSE	MMGS-LIGHT 1	BMGS-DENSE	BMGS-LIGHT 1
ME-MS89L	Sc	20.00	20.00	30.00	20.00
ME-MS89L	Y	34.80	23.00	29.70	15.20
ME-MS89L	La	37.50	38.20	42.00	24.00
ME-MS89L	Ce	54.30	72.80	41.60	89.70
ME-MS89L	Pr	8.89	9.48	9.69	5.61
ME-MS89L	Nd	33.50	33.70	36.80	21.50
ME-MS89L	Sm	5.81	6.71	7.06	3.61
ME-MS89L	Eu	1.42	1.40	1.32	0.71
ME-MS89L	Gd	6.08	5.51	6.30	3.80
ME-MS89L	Tb	1.06	0.86	0.96	0.57
ME-MS89L	Dy	3.88	5.26	3.48	4.32
ME-MS89L	Ho	1.20	0.85	1.08	0.58
ME-MS89L	Er	3.73	2.54	3.38	1.62
ME-MS89L	Tm	0.48	0.37	0.46	0.25
ME-MS89L	Yb	3.56	2.07	2.84	1.62
ME-MS89L	Lu	0.54	0.31	0.45	0.20
TOTAL		216.75	223.06	217.12	193.29

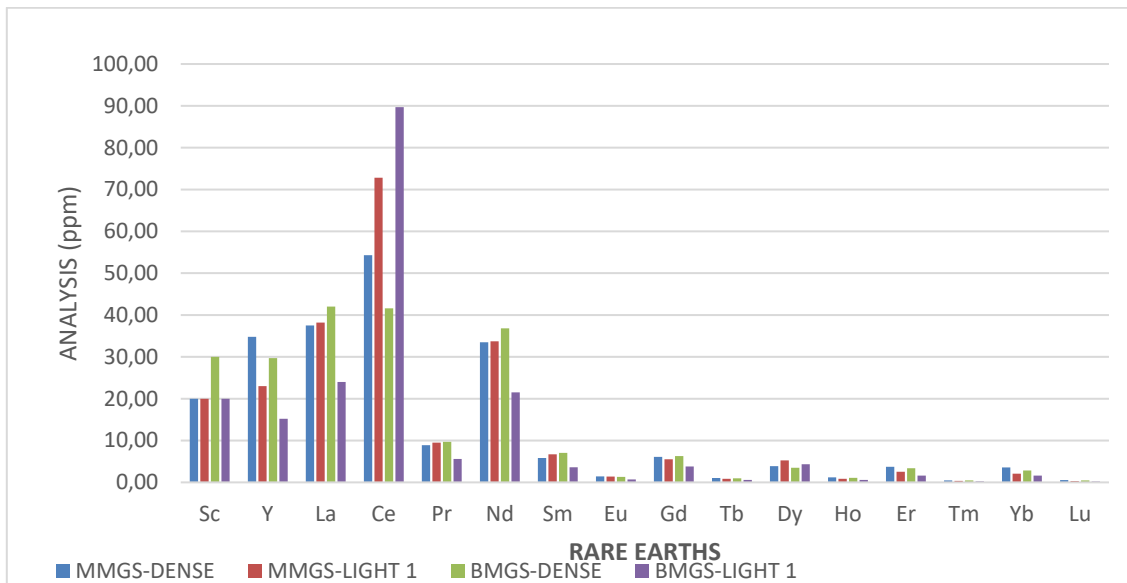


Figure 17-1. Graph of the quantitative analysis (ppm) of the samples obtained by Mozley multigravimetric separation

The results of the percentage analysis obtained from the samples obtained from the Mozley multigravimetric separation (MGS) of La Matona and El Batán with a particle size <0.1 mm are shown in Table 17-2 and Figure 17-2. It can be seen that the results are below the detection limit except for Cerium Oxide (CeO₂) which reaches a value of 0.01%.

Table 17-2. Results of the percentage analysis (%) of the samples from the Mozley multigravimetric separation

METHOD	ELEMENT	SAMPLES (%)			
		MATONA		BATAN	
		MMGS-DENSE	MMGS-LIGHT 1	BMGS-DENSE	BMGS-LIGHT 1
ME-XRF30	La ₂ O ₃	<0.01	0.01	0.01	0.01
ME-XRF30	CeO ₂	0.01	0.01	<0,01	<0.01
ME-XRF30	Pr ₆ O ₁₁	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Nd ₂ O ₃	<0.01	<0.01	0.01	<0.01
ME-XRF30	Sm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Eu ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Gd ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tb ₄ O ₇	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Tm ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Dy ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Ho ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Er ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Yb ₂ O ₃	<0.01	<0.01	<0.01	<0.01
ME-XRF30	Lu ₂ O ₃	<0.01	<0.01	<0.01	<0.01

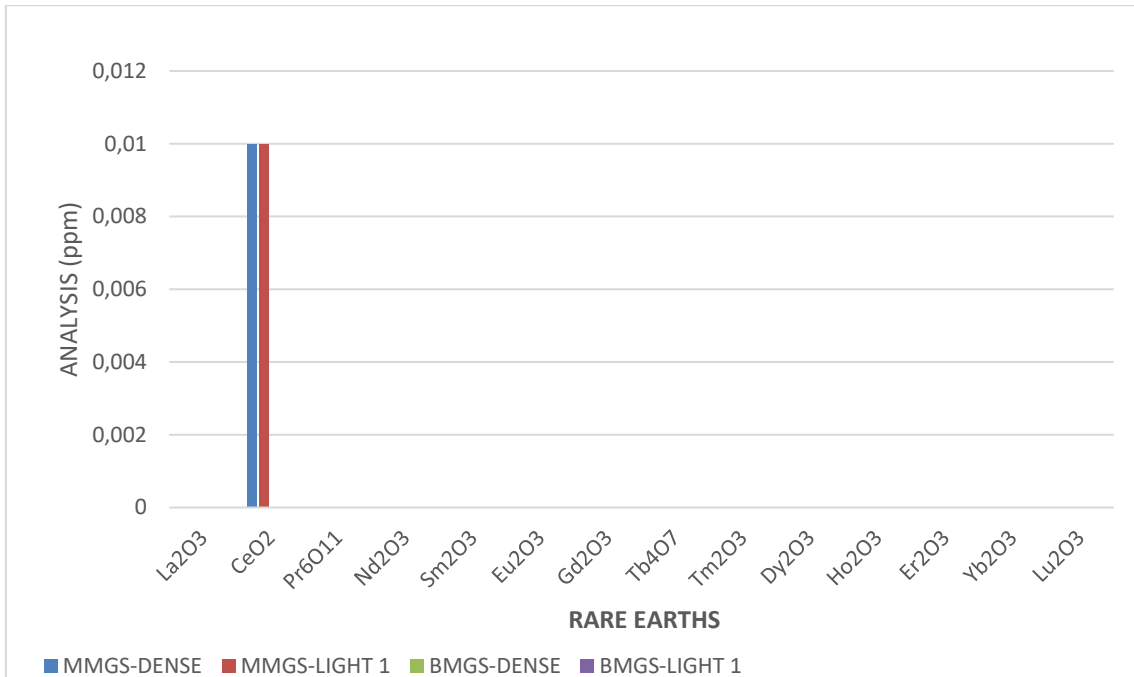


Figure 17-2. Graph of the percentage analysis of the samples obtained by the Mozley muligravimetric separation.

18. Feasibility of rare earths recovery using mineralurgical techniques

As determined by the analyses, TREE concentrations in the coal waste samples ranged from 160 to 220 ppm. Thus, they were generally found to be similar to that of crustal abundance (upper continental crust – UCC), which was estimated at 168.4 ppm by Taylor & McLennan (1985), but higher than values reported for the average content of UA coals, which was estimated at 62.1 ppm by Fikelman (1993). The average REE content for Chinese coals is 137.9 ppm, as Dai et al. (2008) estimated, almost two times that of the USA. To find concentrations about three times higher than the UCC, it is necessary to address coal ashes, as in the case of the USA, which has a concentration of 517 ppm (Seredin & Dai, 2012).

Following the outlook coefficient of REE-rich coal ashes proposed by Seredin & Dai (2012), the average ash samples from the USA fall into Category II: a promising source of raw material for economic development. Thus, coal combustion wastes could be considered as possible sources of REE, as the abundance of metals in ores was between 483 and 621 ppm, according to Seredin & Dai (2012).

Later, according to Wagner & Matiane (2018) and using an updated evaluation plot developed by Dai et al. (2017), ash samples do not qualify as promising when the REE content is below 1000 ppm, a concentration recorded for various deposits globally, due to the costs involved in their enrichment.

Despite all previous studies and analyses, Riesgo García et al. (2017) analysed in deep five ready-to-go rare earths mining projects around the world: Nechalacho Project (North-west Territories, Canada); Zandkopsdrift Project (Northern Cape, South Africa); Bear Lodge Project (Wyoming, USA); Kvanefjeld Project (Southern Green-land); and Dubbo Zirconia Project (New South Wales, Australia). The main purposes being to give an “order of magnitude” both technical and economic of this specific mining industry; to provide a tool for investors, potential investors and professional advisers addressing rare earth mining investment analysis; and to facilitate the development of preliminary economic assessments of future rare earth mining projects. These aims also tried to help to fight against several systemic problems of the rare earth market: lack of trust, market opacity, and short versus long-term approaches and profit orientation.

Regarding the cut-off grades of these projects, only Nechalacho uses an economic cut-off grade: a value that equals the operating costs per tonne of ore, net of estimated metallurgical recoveries and off-site processing costs. Nechalacho’s mineral reserves have a TREO content of 1.7%. Zandkopsdrift uses a physical cut-off grade of 1.0% TREO, Bear Lodge a 1.5% TREO, Dubbo Zirconia a 1.5% combined REO+ZrO₂+Nb₂O₅+Y₂O₃, and Kvanefjeld a 0.015% U₃O₈ as it has greater coverage of assays for uranium than other elements.

Thus, for a mine to be mineable, concentrations of TREO bigger than 1% are required, equivalent to 10,000 ppm. This suggests that the amount of rare earths present in the tailings dumps in the three countries (Spain, Poland, and Slovenia) is too low to be economically viable for exploitation without an adequate concentration process.

This is why we are now focusing on hydrometallurgy recovery; we have started with hydrochloric acid. We will use sulphur, nitric, and organic acids such as acetic and citric acids. We are wondering whether oxalic acid and EDTA could be an option. However, this is out of the scope of the GreenJOBS project.

In conclusion, mineralurgical techniques were demonstrated as inadequate and not economically viable to concentrate rare earths in the tailings dumps in the three countries (Spain, Poland and Slovenia). Moreover, their concentrations are similar to crustal abundance (upper continental crust – UCC) and far from the concentration of other sources, such as some coal ashes, that can qualify as promising (1000 ppm).

Consequently, the technical specifications of these techniques, cost data, and operational constraints were not analysed. Neither was it possible to provide a detailed assessment of the job creation potential, in terms of the production capacity of a rare earth concentration plant, for commissioning and operation.

Conclusions & lessons learnt

In this Deliverable, different approaches for the concentration of mixed rare earth oxides from fine coal waste from the three case studies, Spain (HUNOSA), Poland (WEGLO), and Slovenia (PVM), were undertaken.

The rare earths content and the mineralogical species present were analysed for the initial samples as well as for the different particle size fractions >2.0 mm, 2.0/0.5 mm, 0.5/0.1 mm, <0.1 mm because these are the sizes that would be obtained at various process points in the coal washing plant.

Next, rare earth release and concentration analyses were carried out to decide which methods would allow a higher recovery of rare earth: gravimetric concentration (multi-gravity separator, pulsation box, and shaking table), high-field strength magnetic separation, high-voltage electric field separation, and froth flotation test.

The lessons relevant to the Project from this deliverable can be summarised as follows:

1. Initial preparation of samples usually requires between 3 and 15 days to dry at laboratory temperature so that the next steps can follow.
2. The initial analysis of the samples revealed that quantitative analysis of elements gives much more representative data than the analysis of compounds due to the detection limits of the chosen analytical methods.
3. There are slight differences between the results of the initial samples and the different particle size fractions. This should be since no sampling analyses were made with the initial samples.
4. The rare earths concentration is very similar in the three countries analysed. However, El Batán sample from Spain, which has a high content in coal, has a significant concentration of Ytterbium (Yb) and in Praseodymium (Pr), while a lower concentration of Scandium (Sc), Yttrium (Y), Neodymium (Nd) and Samarium (Sm).
5. Since the analyses performed show very similar rare earth concentrations in the three countries considered, only the possibilities of rare earth concentration in the two Spanish samples were studied in detail. The results are expected to be mostly extrapolated from one waste to another.
6. Pulsation box gravimetric concentration tend to concentrate rare earths in the denser fractions, but nothing really significant.

7. High field strength magnetic separation seems to be the only concentration method that allows a higher recovery of Scandium (Sc), Yttrium (Y), and Cerium (Ce), but only within the fraction 0.1 – 0.5 mm.
8. Rare earth concentrations obtained from analyses range from 160-220 ppm, around 0.016-0.022%, and the possibility of concentrating them by mineralurgical methods is not feasible. For a mine to be mineable, concentrations bigger than 1% (10,000 ppm) are required. This suggests that the number of rare earths present in the tailings dumps in the three countries (Spain, Poland, and Slovenia) is too low to be economically viable for exploitation.
9. We are now focusing as the last option on hydrometallurgy recovery with hydrochloric acid, sulphur nitric acids, and organic acids such as acetic and citric. We also want to know whether oxalic acid and EDTA are options.

Glossary

HREE – Heavy rare earth elements

HUNOSA - Hulleras del Norte S.A.

ICP-AES - Inductively Coupled Plasma-Atomic Emission Spectrometers

LREE – Light rare earth elements

PVM – Premogovnik Velenje MinePV

REE – Rare earth elements

REO – Rare earth oxides

TREE – Total rare earths elements

TREO – Total rare earth oxydes

UCC - Upper continental crust

UNIOVI - University of Oviedo

WEGLO - Weglokoks Kraj Sp. z o.o.

XRF - X-Ray Fluorescence

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