RAWMINA Project

Deliverable 1.1

Mining Waste Characterisation

Collaborative project

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WP	1	Mining Waste Conditioning

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

Summary

Under WP1, several metallic mine waste (MWs) from Spain, Portugal and Chile have been selected within RAWMINA consortium and small quantities chemically analysed at first step. Then four main MWs (tailings and run-off-mine) have been further selected for sampling of bigger amount by 3 sample providers, 1 big-bag of each being prepared for further preparation under WP1. Representative sub-samples have been prepared at BRGM according to established procedures – drying, crushing, grinding, splittering - and delivered to leaching purposes of WP2 (USE and BRGM experiments). Characterisation was performed in three laboratories to evaluate: particle size distribution and composition: pXRF measurements, chemical composition (major, traces) and speciation (C, S) and precise mineralogy by XRD and SEM/EDX.

Two samples concerned altered sulfidic materials very rich in pyrite and containing some metals including CRM: IPB-Tailings1 and IPB-ROM2 (Spain). Another sample named hereafter IPB-ROM1 is a carbonated ROM of Cu-sulfidic deposit containing some Au and with some sulfides and sulphates; it could be used to buffer acidity of bioleaching. The fourth mine waste concern W-tailings2 coming from (Portugal).

Regarding critical raw materials targeted under RAWMINA project (Co, Sb, Ge, W) contents on the 4 MWs are as follow:

- Co: 5-234 ppm; the maximum being for IPB-Tailings1 (also maximum Cu);
- Sb: 7-2355 ppm; the maximum being for IPB-ROM1;
- Ge: <10 ppm;
- W: <50 ppm (3 first samples) and 1857 ppm for W-tailings2.

Mineral processing is currently undertaken on W-tailings2 to concentrate W-bearing minerals and results will be described on D1.2.

Also, two Au-tailings samples from Chile were analysed at first step but not selected a step further because of the presence of CN. A review of Chilean mine context was written instead, and new planning work is proposed.

1. Introduction

Deliverable D1.1. gathers main information on the mine sites and selected mine waste (MWs). Sampling and preparation of MWs are detailed. Methodology and results of characterisation are discussed. Delivery has been 3 months delayed to gathering information on all MWs.

2. Sample description, sampling

A first selection of MWs was given in the proposal. In link with four sample providers in Spain, Portugal and Chile mine waste have been further discussed and selected for analyses and sampling (Table 1). Taking into account bioleaching and alkaline leaching processes that are developed under WP2 of RAWMINA project, selection of mine waste mainly focused on their content in:

- targeted CRM (Co, Ge, Sb, W), base metals, precious metals (Au, Ag);

- sulfides which can generate acidity needed for bacteria development;

- carbonates which can help buffer and control acidity;

Some information on process, volume of waste, particle size distribution, was gathered on a questionnaire. And other traces evaluated such as CN on Chilean samples.

Table 1. List of mine waste studied under WP1

Name	Location	Estimated volume	Information
IPB-tailings1	Spain	14 Mtons	Cu-sulfidic tailings
IPB-ROM1	Spain	3 Mtons	Carbonated ROM, Au
IPB-ROM2	Spain	5 Mtons	Pyrite mine ROM
W-tailings2	Portugal	300 km^3	W-tailings
Au-tailings3	Chile	40 kt	Au-tailings
Au-tailings4	Chile	160 kt	Retreated Au-tailings

2.1.   Site 1 (Spain)

Two samples were selected within the consortium, sampled by sample provider and delivered for preparation of representative samples for the purpose of RAWMINA project: IPB-tailings1 and IPB-ROM1. They concern an active mine on the Iberian Pyrite Belt zone where secondary Cu-sulfides ore was processed: crushed, grinded, HT acid leached before filtering, solvent extraction and electrowinning (SX-EW) to produce grade A copper cathodes. Leached residues called tailings have been stored as a solid cake in the main tailing's facilities.

Sampling for RAWMINA was performed on 200x150 m^2 zone (Figure 1a) by sample provider and a representative sample sent to BRGM without any pretreatment considering the finest of the residues. The stock is evaluated at 14 Mtonnes. Particle size distribution is below <150-200 μm. It is described as a pyritic material (around 80%) containing remaining Cu-sulfides which are not liberated from pyritic grains according to previous MLA results (2017). The sample contains also some Pb and Au.

On the same sector the mineralization of the Cu-deposit comprises an upper layer of iron oxide, overlaying the secondary copper sulfides area mentioned above. This run-off-mine (ROM) is also rich in carbonates – which could be of special interest to buffer acidity during bioleaching step – and contains Pb and precious metals (Au, Ag). Average grade are 3.4% Pb, Au 2.6 ppm, Ag 80 ppm. It contains also some sulfides and sulphates. This ROM is heterogeneous with approximate proportion given as: red oxidized part ~60%; sulfidic part ~40%. 3 Mtonnes are stored on a controlled deposit in a dedicated zone. Sampling for RAWMINA was performed on this area (Figure 1b); the sample was crushed on site before transportation.

a)

b)
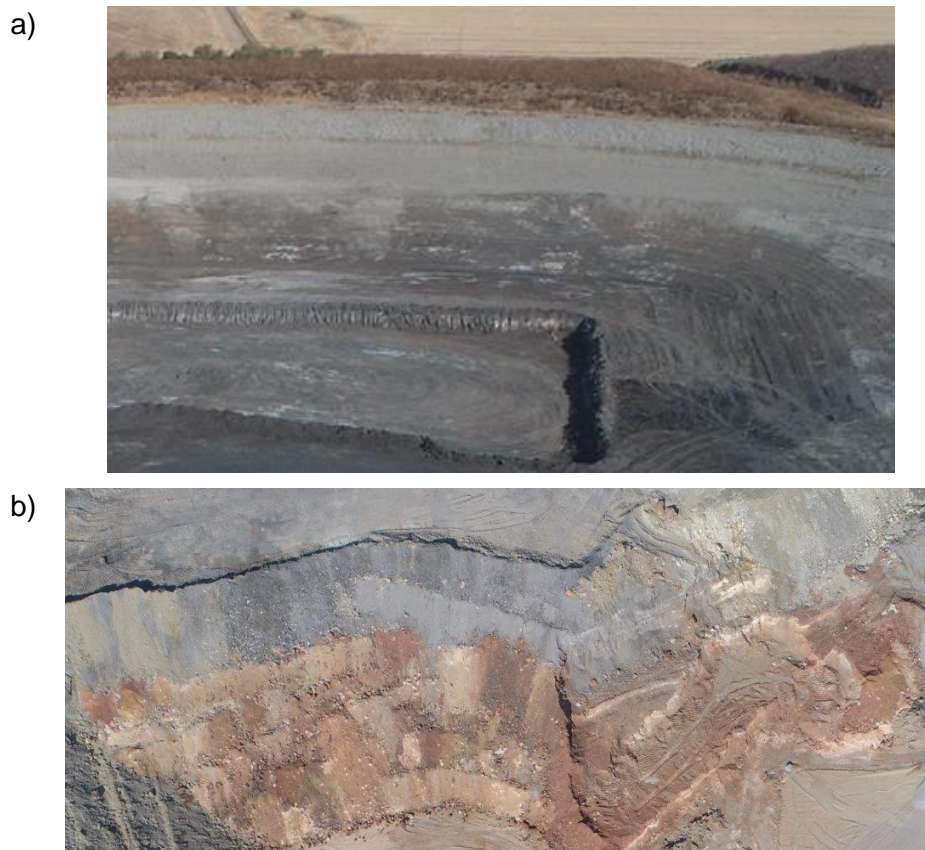
Figure 1. Sampling at site 1: a) IPB-tailings1 and b) IPB-ROM1

2.2. Site 2 (Spain)

Another sample was selected and sampled by a second sample provider (Figure 2) and also delivered for preparation: IPB-ROM2.

a)

b)   c)

Figure 2. IPB-ROM2 sampling: a) general overview of the stock, b) sampling with excavator, c) sampling below 1.5-2m

The sample is a highly weathered run-off-mine (ROM) stock of more than 5 Mtons corresponding to Polymetallic Massive Sulfide ore rejected after crushing due to low pyrite/sulphur content to produce sulphuric acid (less than 45% S). It is located in Spain on the Iberian Pyrite Belt. The stock is heterogeneous from big rocks to fine particles and has been exposed to weather conditions during last 40 – 50 years. It is difficult to beneficiate.

Sampling was performed in September 2021 by sample provider (Figure 2) to collect a 26 tons sample. Sampling grid was established before sampling on site. At each location a hole of 2-3 meters of depth was opened with an excavator and the shovel took different

aliquots (removing the first very weathered 1-1.5 meter) to prepare final composite sample after 4 homogenisation stages.

Finally, one big-bag was sent for preparation. Other big-bags have been stored and are ready to be sent to pilot plant testing (WP6).

Previous work on this stock have been performed last 3 years by the industrial gathering historical data, performing two sampling campaigns on one dump and then develop a model of metal distribution into the stock namely for Co, Au, Cu

2.3.   Site 3 (Portugal)

W-tailings was selected from an old W mine in Portugal exploited by underground mining works which operated during 30 years (1954-1984). This skarn deposit is hosted by schists. Tungsten mineralization was mainly scheelite and minor wolframite associated to massive sulfides (pyrrhotite, pyrite, arsenopyrite and chalcopyrite). The ore was processed through electromagnetic, hydrogravitic, roasting and flotation techniques and tailings disposed on a dedicated site at the end.

Sampling was performed by a sample provider outside of the consortium and transport organised by coordinator LEITAT. Three small samples representing different part of the storage was first sent for first chemical analyses; then one bigger sample was finally selected on the more W-bearing sector using an excavator (Figure 3).

Figure 3. W-tailings sampling (Portugal)

2.4.   Site 4 (Chile)

Two samples from Chile was first selected for preliminary analyses in laboratories. It concerns Au mine waste:

- 40 kt of a mixture of flotation tailings and cyanide process residues;

- 160 kt of fine materials corresponding to a second cyanide operation performed on the first sample to recover Au.

The issue of the presence of cyanide was discussed in relation with WP2 and the development of bioleaching at very low pH. These acid conditions are not compatible with the presence of cyanide and the risk of toxic HCN formation. A first step to destroy cyanide will be needed.

3. Materials and methods

3.1. List of big samples received at BRGM

Big-bags of 4 MW (**Table 2**) were received during the second year-half of 2021 to prepare representative samples for partners.

Table 2. List of mine waste received for preparation at BRGM (big samples)

Name	Date of reception	Quantities
IPB-tailings1	2021, July 13th	851 kg
IPB-ROM1	2021, July 13th	1053 kg
IPB-ROM2	2021, Sept. 30th	905 kg
W-tailings2	2021, Sept. 23rd	586 kg

3.2. Materials for sample preparation

Jaw crusher

The jaw crusher used is an EB 200 x 125 L crusher from SIEBTECHNIK (Figure 4), it consists of a fixed jaw and a mobile jaw. The spacing of the crusher jaws is adjustable, its amplitude is from 2 mm to 50 mm.

Figure 4. Jaw chrusher Siebtechnik (@BRGM)

Figure 5. Cone crusher (@BRGM)

Cone crusher

The cone crusher used is a KM65 from SIEBTECHNIK (Figure 5). The size of the slot between cone and ring can be adjusted as required, its amplitudes is from 2 to 10 mm.

Rod mill

The rod mill used is a 72 L mill, (DxL: 450 x 455 mm), the rods used have diameters of 22 mm and 26. The rotational speed is 43 rpm (Figure 6).

Figure 6. Rod mill (@BRGM)

Four-way rotary splitter

The four-way rotary splitter is home-made splitter (Figure 7). The feed sample is fed at a controlled rate with a hopper and a conveyor belt. The conveyor belt speed and splitter rotary speed are adjustable. The feed particle size is between 50 µm to 200 mm. This device is used for sample mass between 100 kg to several tonnes.

Figure 7. Four-way rotary splitter (@BRGM)

Riffle splitter

Laboratory splitting are made with manual two-ways splitters (riffle splitter). Three different size splitters are used (Figure 8).

Figure 8. Riffle splitters (@BRGM)

Sieving

Samples were sieved in wet condition through 40 µm, 63 µm, 125 µm, 160 µm, 250 µm, 500 µm and 1 mm sieves. For characterisation purpose, vibratory lab-sieve shaker was used. For mineral processing tests a multi-deck screening machine (ROTO Sieve D=400 mm) was used.

3.3. Chemical measurements and analyses

3.3.1. Chemical measurement by portable XRF (p-XRF)

Chemical measurements were performed at BRGM by portable XRF (pXRF) technique to evaluate content of some elements and namely compare size fraction. The technique is less precise than chemical analyses in laboratories.

3 g of sample was manually pressed into a 26 mm cupule. Free space remaining was filled with cotton. The pellet cupule was closed with a 6 μm Mylar film. The analysis was performed using a Thermo NITON XL3T 900 with mining mode. Time measurement was 30 seconds for each filter. Quantification was performed with calibration implemented in the apparatus.

3.3.2. Chemical analyses

Each mine waste was extensively analysed by AGQ laboratories on:

- A raw 1 kg aliquot directly sent to AGQ facilities (8 samples) at the beginning of the project by sample providers; to precise rapidly content range before final sampling;
- A representative 1 kg aliquot of homogenised samples prepared at BRGM for the full project and concerning 4 big samples (Table 2).

Methods are detailed on Table 3.

Analyses of homogenised samples are those discussed in this report and to be considered in next steps of the project.

Table 3. Chemical analyses performed by AGQ

Type	Method	List of elements
Major and trace elements	'Near total digestion' – four acids digestion (HF, H_3ClO_4, HNO_3, HCl) ICP-OES (Agilent 5110 with axial and radial view) - Uncertainty 10%	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sn, Sr, Ti, Tl, V, W, Zn.
Rare-earth elements - REE	Four acids digestion with ultra-pure acids ICP-OES (Agilent 5110) Uncertainty 30%	Ce, Dy, Er, Eu, Gd, Ho, Ho, La, Lu, Nd, Pr, Pr, Sc, Sm, Tb, Th, Tm.
Au	Fire assay (30-50 g), ICP-OES (Agilent 5110) - Uncertainty 10%	Au
Total Carbon (TC) Organic Carbon (IC)	Acid attack of carbonate or not (total C), calcination around 1350 °C with O2 and reagent, IR quantification of CO2 (LECO, CS744)	C

Type	Method	List of elements
Inorganic Carbon (IC)	Pyrolitic pretreatment with O2 (2 h) before total C procedure / or calculated	C
Total Sulphur (TS)	Calcination around 1350°C with O_2 and catalyser, IR quantification of SO_3 (LECO CS744)	S
SO_4^{2-}	Pyrolytic pre-treatment with O_2 (2 h) to remove S-Sulphide before total S procedure	SO_4^{2-} or $S(SO_4^{2-})$
Other S (than SO_4)	Leaching by Na_2CO_3 to precipitate sulphates, filtration, washing, Leco	$S(S^{2-})$
Total CN	EPA METHOD 9013	CN
Weak Acid Dissociable Cyanide (WAD CN), free CN	Leaching with different acid (increase strongness) and EPA Method 9013	CN

3.4. Mineralogical methods

Several techniques have been used to evaluate mineral phase and speciation of metals (Table 4).

Table 4. Mineralogical studies on mine waste

Name	Samples	Materials
IPB-tailings1	Raw, particle size fractions (wet)	XRD, SEM/EDX
IPB-ROM1	Raw, particle size fractions (wet)	XRD, SEM/EDX
IPB-ROM2	Raw	XRD, SEM/EDX

4. Results: IPB-tailings1

4.1. Preparation of mine waste

Figure 9 displays the overall material conditioning and sampling undertook for IPB-tailings1.

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          ┌─────────────────────┐
          │   tailings sample   │
          │   (wet, 851 kg)     │
          └─────────────────────┘
                     │
                     ▼
          ┌─────────────────────┐
          │      Drying         │
          │  Oven at 40°C (72h) │
          └─────────────────────┘
                     │
                     ▼
          ┌─────────────────────┐
          │      Crushing       │
          │    Cone crusher     │
          │    (CSS = 5 mm)     │
          └─────────────────────┘
                     │
                     ▼
          ┌─────────────────────┐
          │  Material blending  │
          │   (dry, 791 kg)     │
          └─────────────────────┘
                     │
                     ▼
          ┌─────────────────────┐
          │  Four-ways rotary   │
          │      splitter       │
          └─────────────────────┘
                     │
```

Sample A	Sample B	Sample C	Sample D
Net weight = 190 kg	Net weight = 202 kg	Net weight = 195 kg	Net weight = 193 kg

```
          ┌─────────────────────┐
          │  Four-ways rotary   │
          │      splitter       │
          └─────────────────────┘
                     │
                     ▼
          ┌─────────────────────┐
          │     32 samples      │
          │ Net weight = 45-50 kg│
          │       each          │
          └─────────────────────┘
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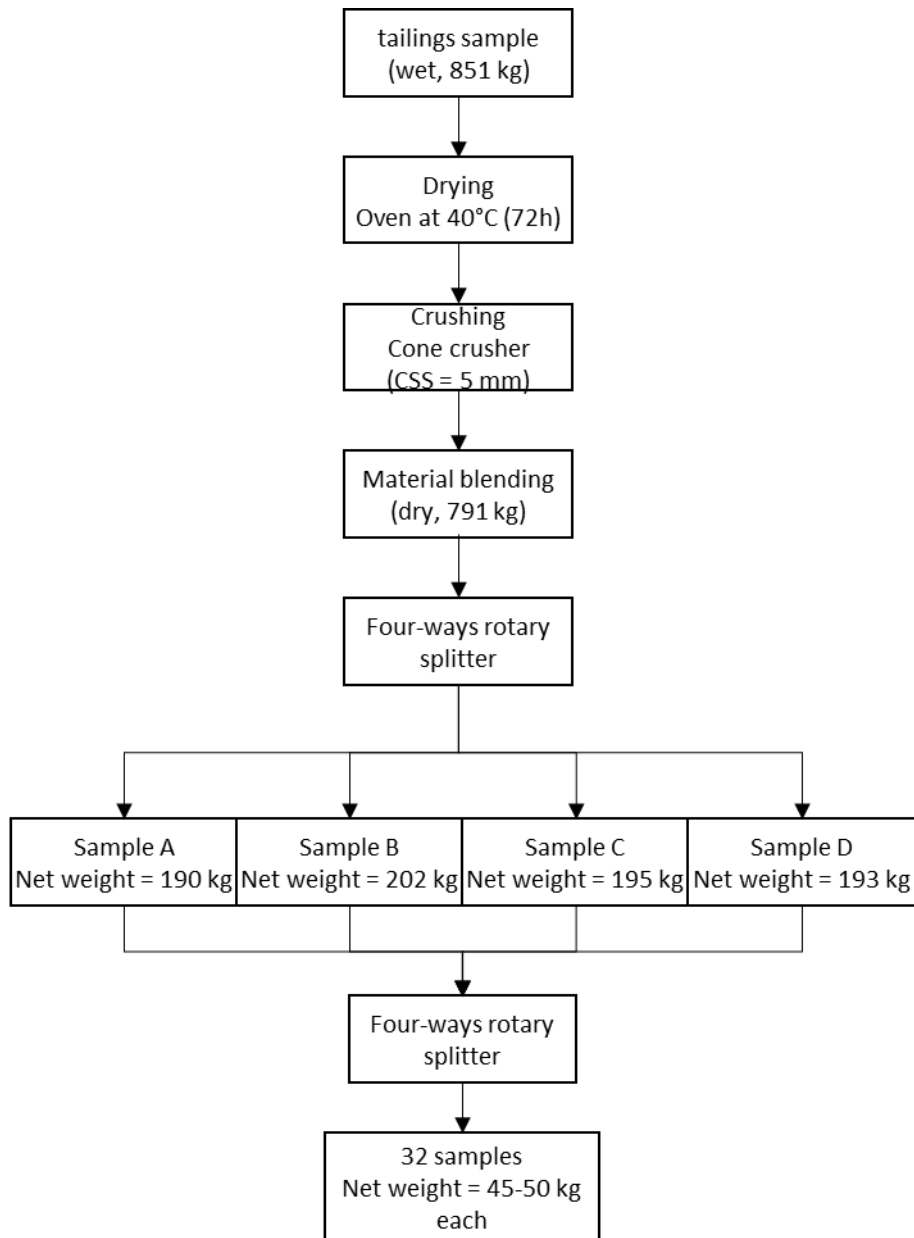
Figure 9. IPB-tailings1: preparation procedure

First of all, this material was placed on trays and then dried in oven at 40° C for 72h (Figure 10) in order to undertake afterwards its sampling. Given the agglomeration of the material while drying, a pulverizing step was also implemented ahead of sampling using a cone crusher with a closed setting side of 5 mm (Figure 11).

Then, the sampling procedure consisted in using a four-way rotary splitter to produce four sub-samples of approximately 190-200 kg each. The rotary splitter is used a second time for each of them to produce ultimately 32 samples of approximately 45-50 kg each.

Figure 10. IPB-tailings1: picture of drying (@BRGM)

Figure 11. IPB-tailings1: picture of crushing after drying using a cone crusher (@BRGM)

Table 5 summarizes samples provided by BRGM to the project partners.

Table 5. IPB-tailings1: delivery of sub-samples to partners

IPB-tailings1	Dedicated for	Weight (kg)	Amount
USE	Lab scale bioleaching tests – different sub-samples for labscale experiments	0.1	20
		0.25	20
		1	20
		20	1
	Pilot scale bioleaching tests (stored)	20	10
AGQ	Chemical analysis	1	1
UAB	Mineralogical analysis	0.2	2
BRGM	Chemical analysis per size fraction	0.5	4

IPB-tailings1	Dedicated for	Weight (kg)	Amount
	Lab scale bioleaching tests - different sub-samples for labscale experiments	0.003	20
		0.1	4
		0.2	10
	Pilot scale bioleaching tests	20	20

4.2. Chemical composition

Fe-sulfidic material type is confirmed for (35.3% Fe; 37.6 % S as sulfides) in association with altered sulphate phases. Tailings contain Cu (2.2%) and some other metallic/ metalloid trace elements such as Pb (8900 ppm), As (4200 ppm). Precious metals analyses give: 0.7 ppm Au and Ag 48 ppm. RAWMINA targeted CRM are: 234 ppm Co, 432 ppm Sb, Ge and W being below detection limits (<10 ppm and <50 ppm respectively).

4.3. Particle size distribution (wet), composition, pH

500 g of sample was stirred in 1.5 L water during 4h and pH was measured. The obtained solution is blue in relation with Cu-minerals dissolution. pH is low: pH2.75 at 22.8° C.

Wet sieving has been carried out on the product received without any preparation. The percentages of chemical elements measurements by p-XRF in different size fractions of the IPB-tailings1 are presented in Table 6 for comparison. Fine particle size distribution is confirmed with around 64% below 40 µm after dissolution of some mineral phases.

Table 6. IPB-tailings1: particle size distribution (wet); Cu. Fe. Co. W. Pb and Sb contents (pXRF)

Particle size	Distribution	Cu	Fe	Co	W	Pb	Sb
µm	% mass	%mass	%mass	ppm	ppm	ppm	ppm
>125	3.7	0.4	9	220	26	1595	265
63-125	17.5	0.9	31	< LOD	163	1865	374
40-63	15.2	1.4	30	445	172	1997	349
<40	63.6	1.9	29	< LOD	278	14115	724
Calculated	100	1.6	29	-	233	9663	588
Raw Material		2.3	25	424	175	9586	537

LOD = limit of detection – not evaluated precisely (Co)

Fe is "homogeneously" distributed among the various particle size except the coarser one (> 125µm). Considering the high proportion of fine particles and concentration of Cu. W. Pb and Sb these elements are concentrated in the fine fraction (< 40 µm).

4.4. Mineralogy

Table 7 summarises the results of characterisation by X-Ray Diffraction (XRD) and Scanning Electronic Microscopy (SEM/EDX).

Table 7. IPB-tailings1: main mineral phases

Type	Main mineral phases By XRD (UAB)	Microscopy (grain size) SEM observation and EDX analyses (BRGM)
Sulfides	XRD estimation: 30 % pyrite	Fe/S - pyrite (py) main sulfide Simple Cu-sulfide: Cu/S Complex Cu-sulfide: Cu/Fe.As/S
Sulphates	XRD estimation: 50 % gypsum	Ca-sulphate: Ca/S/O Fe-sulphate: Fe/S/O (Cu) Pb-sulphate: Pb/S/O
Quartz	XRD estimation: 10 % quartz	Si/O (SiO_2)

XRD allows to identified main crystalline mineral phases and estimate their proportion. The main crystallised mineral phases evaluated by XRB at UAB are as follow: gypsum (>50%). FeS_2 (>30%). quartz (~10%) + others <5%.

XRD of wet size fractions show the same mineral phases with different porportions. gypsum being more or less leached. No other sulfides than pyrite were determined. Fine fraction <20 μm contains hydrated Cu-sulphate of the type $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$ Wroewolfeite.

Punctual SEM/EDX analyses (Figure 12) allows identifying the same main crystalline phases (gypsum, pyrite and quartz) and in addition:

- very poorly crystalline such as Fe-sulphates (with some Cu) and Pb-sulphate;

- minor phases (generally below 1-5%) such as Cu(Fe.As)-sulfides present in complex mixed grains and in association with pyrite.
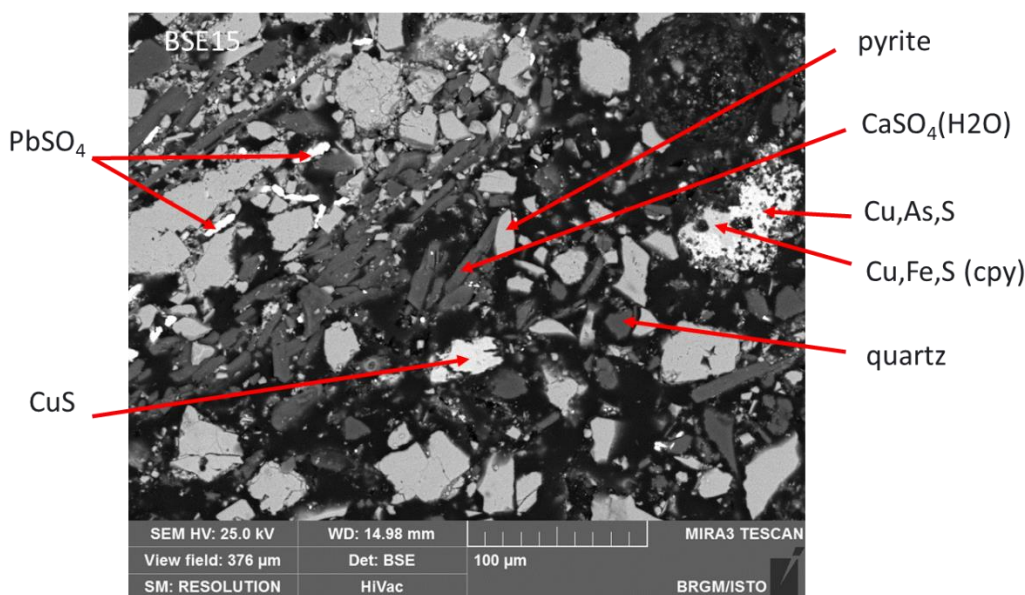
Figure 12. IPB-tailings1: SEM/EDX (@BRGM)

Cu-sulfides can be of different type: simple Cu-sulfides and in association with Fe (chalcopyrite) or As (tennantite and/or enargite).

These results are consistent with MLA results obtained on a leached sample in 2017 by sample provider (thus poorer in Cu: 0.7 % against 2.2% and without gypsum that have been put into solution). Pyrite was the main mineral (80 %), the sample also containing also quartz (15 %) and complex Cu-sulfides: enargite accounting for 63% Cu >> chalcopyrite and tennantite accounting for 12 % and 16 % Cu. Others Cu-sulfides accounted for less than 5 % each were also determined: simple Cu-sulfides that have been partly leached (covelite. chalcocite) and tetrahedrite being the main Sb-carrier and also containing Ag. Another result was that Cu-sulfides are poorly liberated and mainly associated to pyrite that need to be attack to leach Cu.

Co was not evaluated because below detection (<0.1 %); Sb (0.2 %) is mainly linked to tetrahedrite (90%); As (0.29 %) to enargite (63 %), dufrenosite ($Pb_2As_2S_{25}$) and tennantite (18 % each); Pb (1.14 %) is associated to galena (32%) and other minerals in gangue; Zn (0.32 %) is associated to sphalerite (98 %).

5. Results: IPB-ROM1

5.1. Preparation of mine waste

About one tonne of IPB-ROM1 sample (Run Of Mine) material filled into two big-bags was delivered at BRGM after crushing on-site. Figure 13 displays the overall material conditioning and sampling undertook.
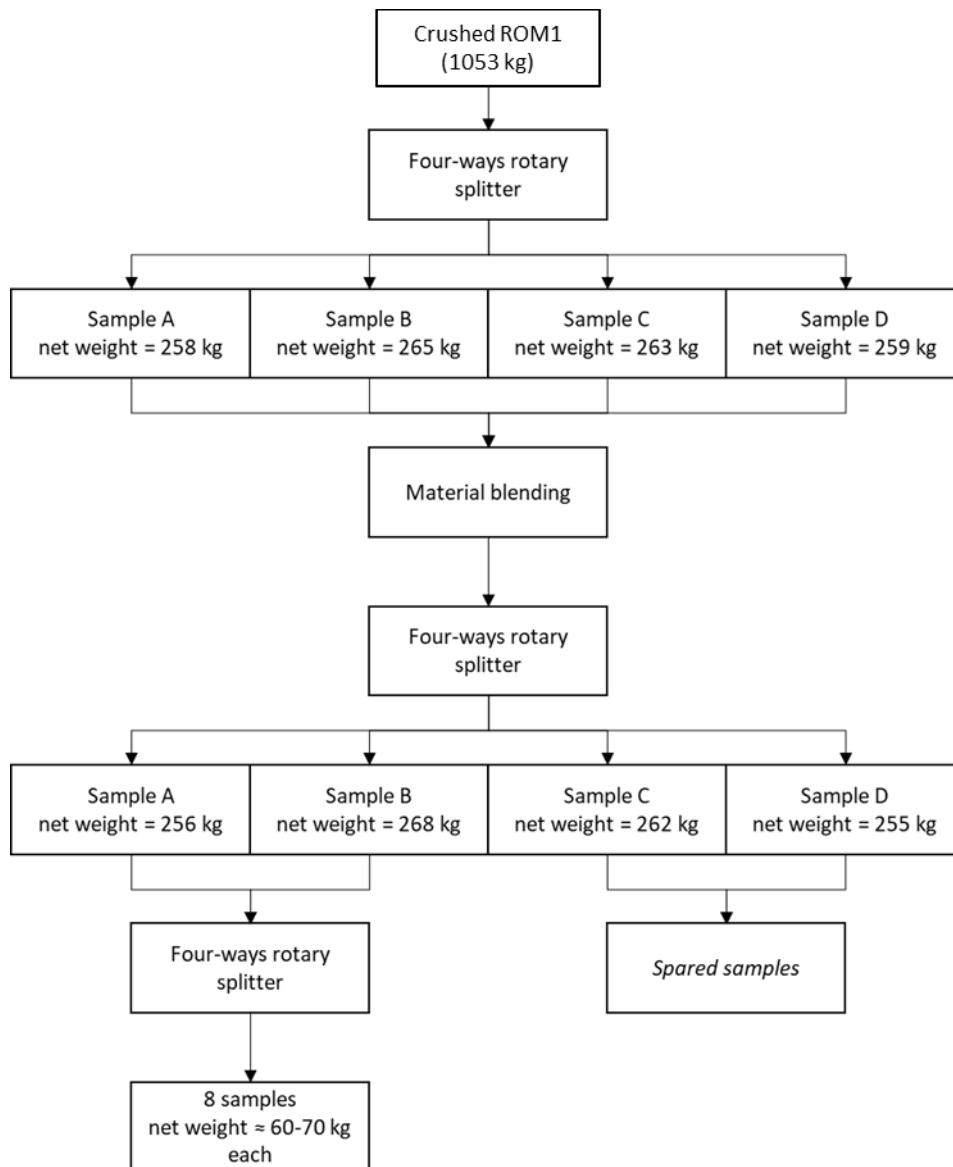

Figure 13. IPB-ROM1: preparation procedure

This material was previously crushed at sample provider site to reach a top size of about 10 mm. To ensure the material homogeneity ahead of sampling both big-bags were

emptied into a hopper then feeding a four-way rotary splitter. Every split samples were then blended again into the feed hopper. Afterwards, the sampling procedure (Figure 14) undertook brought in the four-way rotary splitter twice to produce eight samples of approx. 60-70 kg each while the two remaining 250-260 kg samples were spared for further use.

Figure 14. IPB-ROM1: pictures of the preparation of sub-samples (@BRGM)

Further sampling to come with smaller samples was conducted using a manual two-ways splitter. Table 8 summarizes samples provided by BRGM regarding IPB-ROM1 material among the project partners.

Table 8. IPB-ROM1: delivery of sub-samples to partners

| IPB-ROM1	Dedicated for	Weight (kg)
AGQ	Chemical analysis	1
UAB	Mineralogical analysis	0.4
BRGM	Chemical analysis per size fraction	2
USE	Bioleaching tests	5

5.2. Chemical composition

IPB-ROM1 is a carbonated material (1.57 % C inorganic expressed as $CaCO_3$ is 13 %) also containing sulfides and sulphates. It contains base metals: 4.17 % Pb and 1700 ppm Cu. Precious metals analyses give: 2.9 ppm Au and 85 ppm Ag. Targeted CRM are as: 11 ppm Co. 2355 ppm Sb. Ge and W being below detection limits (<10 ppm and <50 ppm respectively).

5.3. Particle size distribution

Table 9. IPB-ROM1: particle size distribution (wet)

Fractions	Recovery wt%
-63 µm	27.0
250-63 µm	8.9
500-250 µm	6.9
1.25mm-500 µm	10.1
2-1.25 mm	7.4
4-2 mm	14.4
+4 mm	25.4
	100
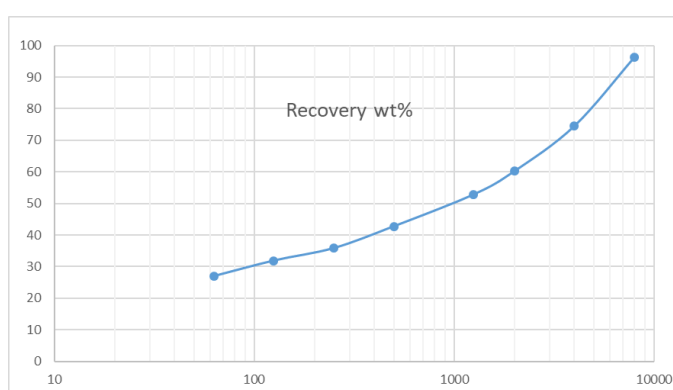
Wet sieving has been carried out on the product after mm crushing in order to evaluate namely the distribution of carbonates, sulphates and Au. Data are shown on Table 9.

5.4. Work index

The sample was ground below 106 µm and Bond ball mill work index measured by sample provider at 7.5 kWh/tonne.

5.5. Mineralogy

Table 10 summarises the results of characterisation by X-Ray Diffraction (XRD) and Scanning Electronic Microscopy (SEM/EDX).

XRD allows to identified main crystalline mineral phases and estimate their proportion. The main crystallised mineral phases evaluated by XRB at UAB are as follow: FeS2 (>50%), FeSO4·xH2O (~35%*), quartz (~15%) with various monoclinic iron sulphate hydrate phases present.

SEM images (Figure 15) and EDX analyses identified the same main phases and also minor phases (generally below 1-5%) or very poorly crystalline. Namely, sulfides such

as galena, pyrite and mixed sulfides Sb/Pb(Bi) were analysed; sulphates such as barytine and Fe-sulphates containing Pb. Sb (Bi); Fe oxy-hydroxide containing traces such as Sb. Pb. Ti.

Table 10. IPB-ROM1: mineralogy

| Type	Main mineral phases By XRD (UAB)	Microscopy (grain size) SEM observation and EDX analyses (BRGM)
Sulfides	XRD: sulfides not detected ;	Fe/S - pyrite (py) Pb/S – galena (gn) Mixed sulfides: Sb/Pb/S(Bi); Pb/S(Sb)
Sulphates	XRD estimation: 10 % gypsum XRD estimation: 5 % anglesite	Ca/S/O Ca-sulphate $PbSO_4$ anglesite $BaSO_4$ barytine Fe/S/O + Pb. Sb(Bi)
Oxides	XRD estimation: 5 % hematite	Fe/O (low traces) – hematite Fe_2O_3 Fe/O + Sb.Pb.Ti.S.etc – oxy-hydroxide
Carbonate	XRD estimation: 15 % calcite	Ca/C/O ($CaCO_3$)
Quartz	XRD estimation: 60 % quartz	Si/O (SiO_2)
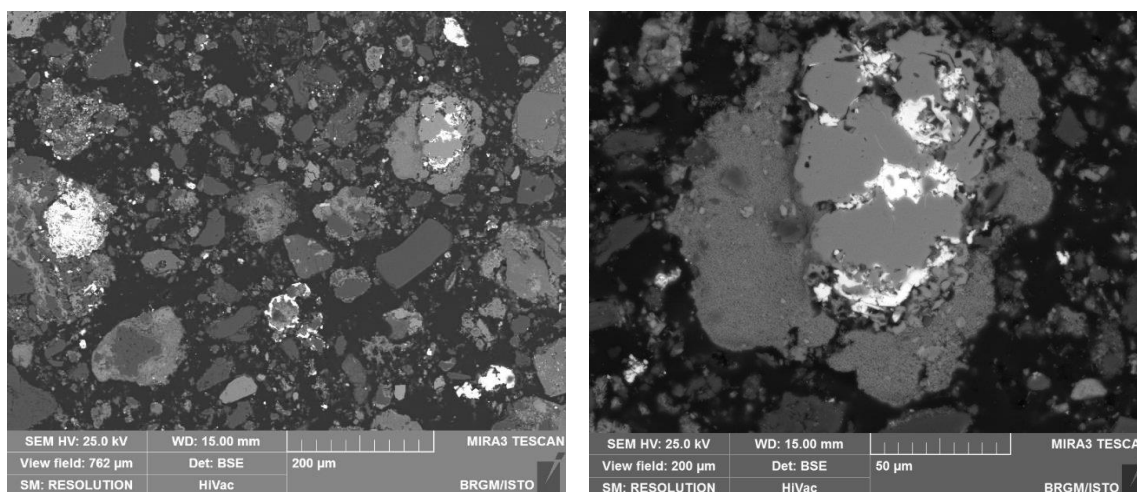
Figure 15. IPB-ROM1: backscattered SEM images (@BRGM)

6. Results: IPB-ROM2

6.1. Preparation of mine waste

BRGM received one big-bag from sample provider filled with about 900 kg of rejected polymetallic ore from the mine site including large size material up to approximately 300 mm. Ahead of the sampling procedure undertook at BRGM the ore preparation included manual size scalping (for +400 mm and +200-400 mm ore blocks), blending and several crushing steps (Figure 16).

Following the last crushing step (CSS = 4 mm), the ore material underwent a two-stages sampling procedure using a rotary four-way splitter (Figure 18). The outcome was the production of 8 samples of approx. 50-60 kg each plus two remaining samples of approx. 210-220 kg spared for further sampling if necessary.

This sampling procedure was then followed with a third sampling step using a manual two-ways divider for each 50-60 kg samples, providing thus with 16 samples of approx. 25-30 kg of ore material each.
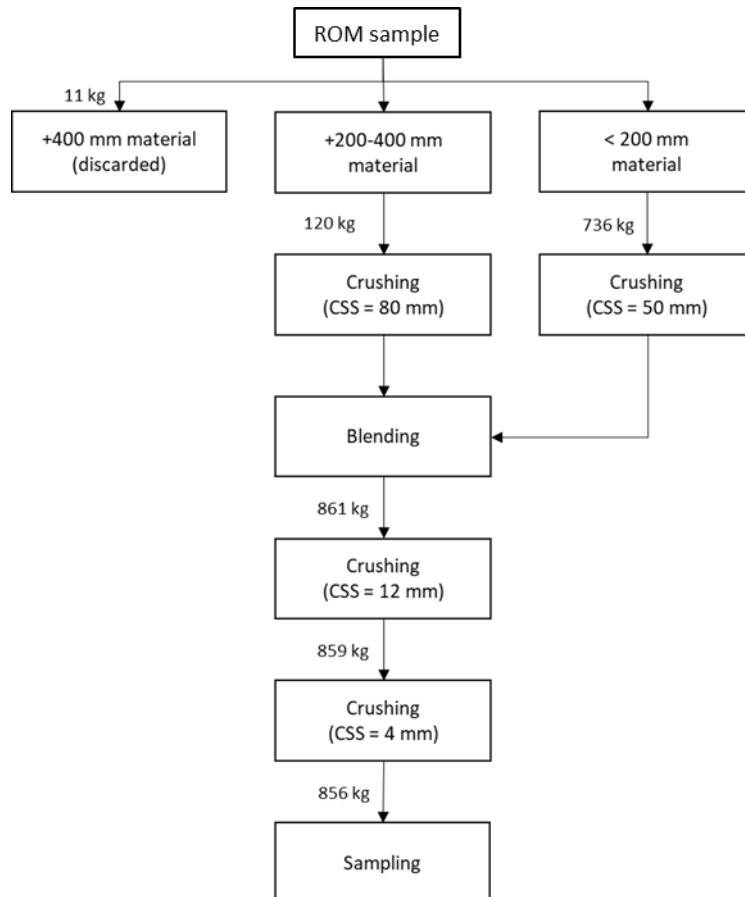

Figure 16. IPB-ROM2: preparation procedure

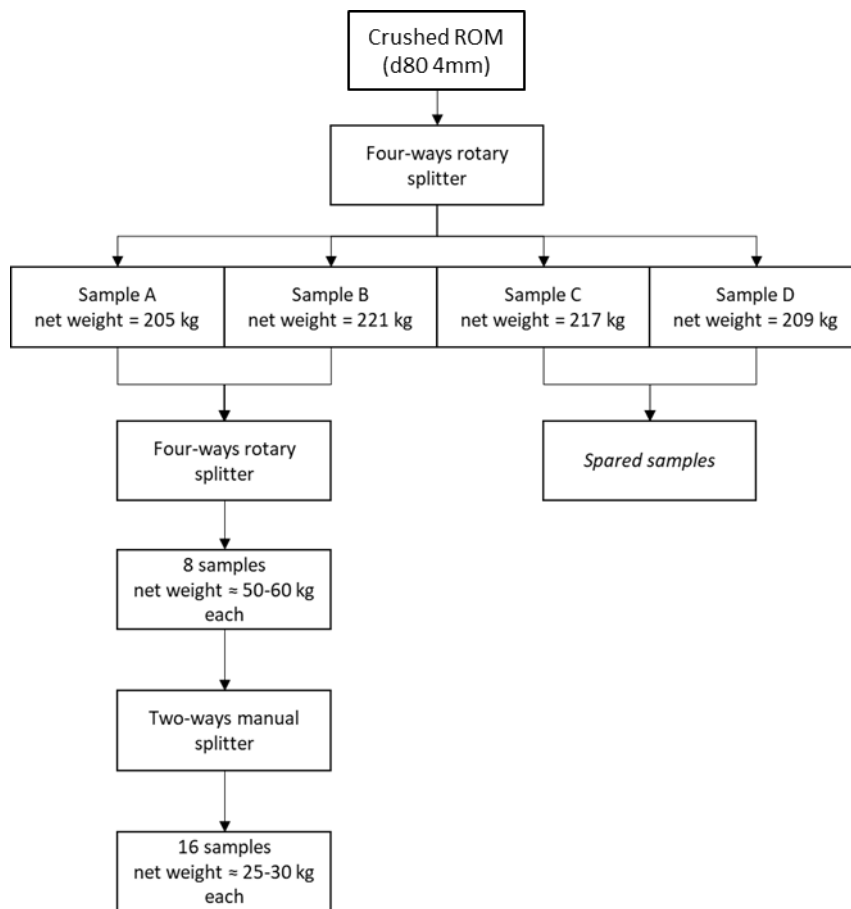Figure 17. IPB-ROM2: pictures of the material preparation at BRGM (@BRGM)

Figure 18. IPB-ROM2: sub-samples preparation procedure

In the perspective of WP2 experiments, target size has been defined with by downstream partners depending on their process requirements. Several samples of 25-30 kg underwent further grinding to reach a size particle below 100 µm.

The grinding procedure is illustrated on Figure 19 and brought in a cone crusher with an adjustable CSS set between 1 and 4 mm. Then, dry rod milling and dry sieving with a mesh size at 125 microns were implemented in order to reach the aimed d80.
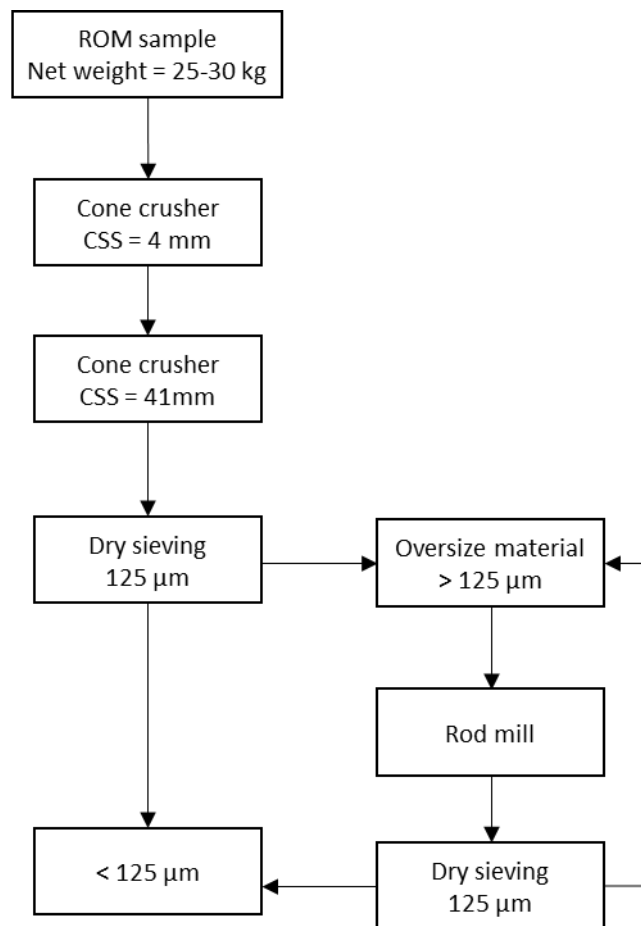

Figure 19. IPB-ROM2: grinding procedure

The laboratory rod mill charged with 152 kg of 22 mm and 26 mm diameter rods and 10 kg of <1mm test sample was used for final grinding. The grinding time was 30 min.

Table 11. IPB-ROM2 (ground): delivery of sub-samples to partners

IPB-ROM2	Dedicated for	Weight (kg)
USE	Lab scale bioleaching tests Ground sample (< 100 µm) – 7 bags of 5kg	35
AGQ	Chemical analysis	1
UAB	Mineralogical analysis	0.4
BRGM	Chemical analysis per size fraction	2
USE / BRGM	Lab scale bioleaching tests Ground sample (< 100 µm)	35

Table 11 summarizes samples needs provided by BRGM regarding IPB-ROM2 material among the project partners.

6.2. Chemical composition

Figures of homogenised samples are discussed hereafter.

MW sample is a Fe-sulfidic material (35.3 % Fe; 30.9 % S as sulfides) containing some altered sulphate phases. It contains base metals: 7600 ppm Pb, 6600 ppm Zn and 3000 ppm Cu and some other trace elements such as As (2000 ppm). Precious metals analyses give: 1.1 ppm Au and 27 ppm Ag. Targeted CRM are: 178 ppm Co, 451 ppm Sb, 11 ppm W, Ge being below detection limits (<10 ppm).

## 6.3. Particle size distribution (wet)

Particle size distribution on wet condition was performed twice on the ground samples that will be used in WP2 and WP5 experiments: on the sample sent to USE and the one of BRGM. Results are comparable (Table 12). Losses represent 23-24 wt % in relation with large mineral dissolution, namely associated to Fe-sulphates. d80 are 62-64 µm similar to IPB-tailings1. Mass distribution of the samples show that finest fractions (<40 µm) are predominant (70%) with a d80 around 64 µm.

Measured pH are 3.2 (16.1° C) and 3.04 (16.6° C) respectively – 500 g in 1.5 L water.

Table 12. IPB-ROM2 (ground): particle size distribution (wet). d80. pH

Fractions	BRGM sample wt%	USE sample wt%
+250 µm	0.1	0.1
+160-250 µm	0.4	2.6
+125-250 µm	1.6	0.8
+63-125 µm	18.5	16.2
+40-63 µm	9.1	7.4
< 40 µm	70.4	73.0
loss	24.0	22.8
d80 (µm)	64	62
pH	3.04	3.2
T°C	16.6	16.1
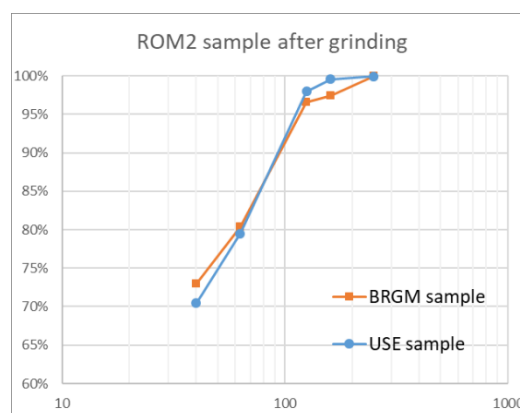
6.4.   Work index

Bond ball mill work index was measured previously by sample provider on a similar sample: 22.26 kWh/ton.

6.5.   Mineralogy

Table 13. IPB-ROM2: main mineral phases

Type	Main mineral phases By XRD (UAB)	Microscopy (grain size) SEM observation and EDX analyses (BRGM)
Sulfides	XRD estimation: > 50 % pyrite	Fe/S - pyrite (py) Zn(Fe)/S – sphalerite Pb/S – galena Cu/Fe/S – chalcopyrite Fe/As/S – arsenopyrite (minor)
Sulphates	XRD estimation: 35% $FeSO_4.xH_2O$ (x. various hydrated degree)	Pb-sulphate (Fe) - anglesite Fe/S/O + Mg. Mn. Zn
Oxides		Fe(Mg)/O
Quartz	XRD estimation: 15 % quartz	Si/O (SiO2)

Table 13 summarises the results of characterisation by X-Ray Diffraction (XRD) and Scanning Electronic Microscopy (EM/EDX).

XRD allows to identified main crystalline mineral phases and estimate their proportion. The main crystallised mineral phases evaluated by XRB at UAB are as follow: FeS_2 (>50%), $FeSO_4 \cdot xH_2O$ (~35%) – x representing different hydration degree - , quartz (~15%).

Distinct proportions are given by sample provider on another sample (previous project) that appeared more weathered: 20% pyrite. 70% complex Fe-sulphates, 1.1% blende, 0.7 % chalcopyrite, 0.2 % galena and 8% of other minerals. Pyrite liberation after milling to P80 of 110 µm was also estimated: at this grain size, i.e. 25 wt % of pyrite is 90-100 % liberated, other 30 % is 70-90% liberated.

SEM image (Figure 20) and punctual EDX analyses identified the same main phases and also minor phases (generally below 1-5%) or very poorly crystalline. Namely. sulfides such as galena, pyrite, chacopyrite and arsenopyrite (very limited) were analysed; and also Pb-sulphates.
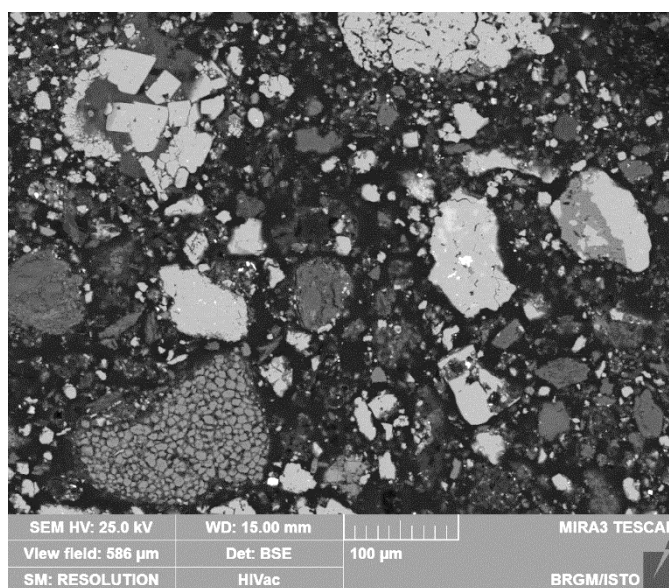

Figure 20. IPB-ROM2: SEM image (@BRGM)

7. Results: W-tailings

7.1. Preparation of mine waste

BRGM received one big-bag filled with about 600 kg of tailings from mine site in Portugal. The sampling procedure undertook at BRGM for this material brought in a four-way rotary splitter twice to provide with two samples of about 70 kg each (Figure 21). Most of the tailings appears sand grain-sized, excepted for larger and indurated agglomerates (Figure 22). This material being still a bit wet, these samples were then dried in oven at 40° C ahead of conducting their particle size reduction.
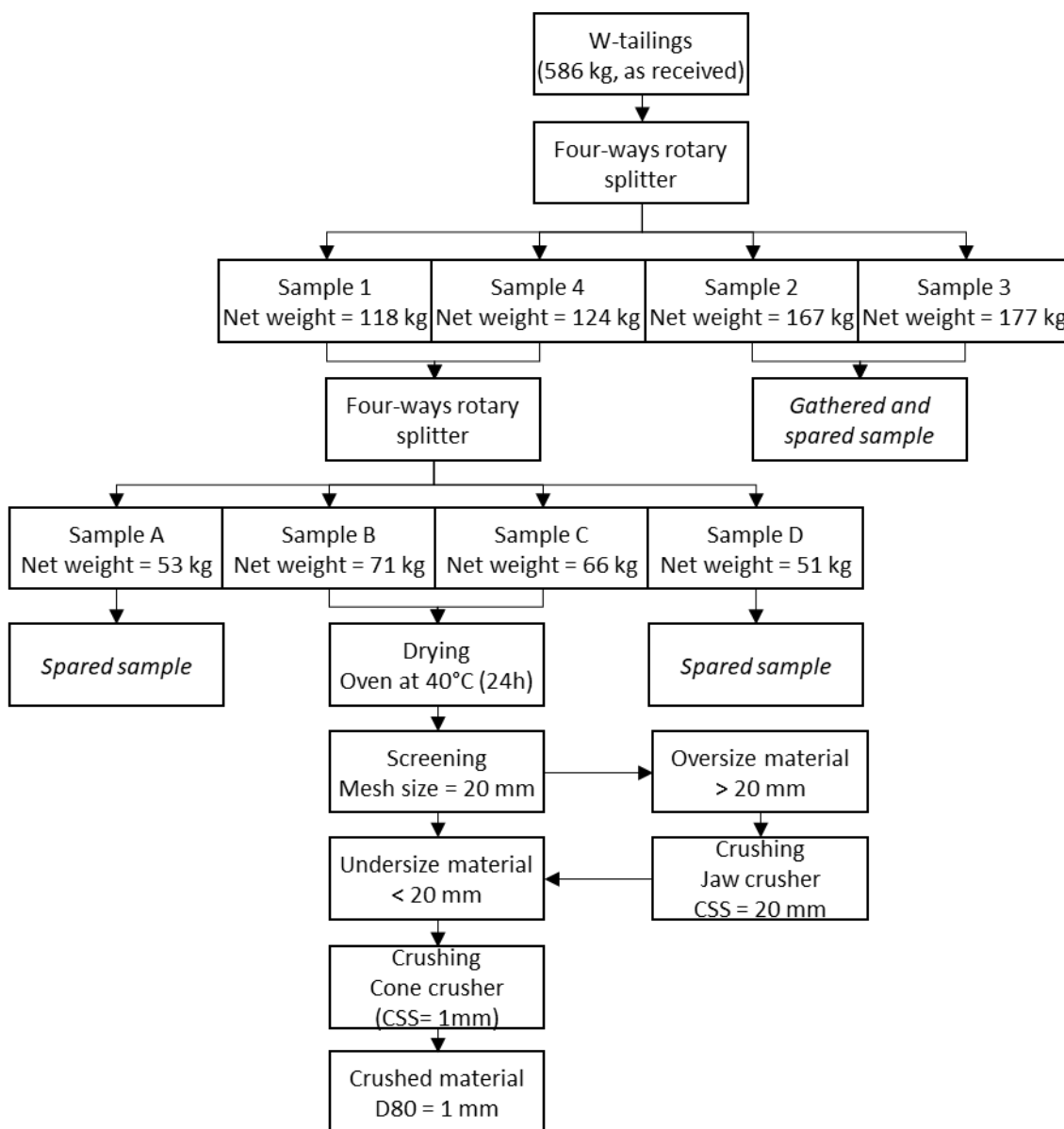
Figure 21. W-tailings: preparation procedure

Once dried, the two samples of approx. 65-70 kg underwent a comminution path including screening at 20 mm, with the oversize material being crushed using a jaw crusher. Finally, a cone crusher (CSS = 1 mm) was used to further comminute the sample ahead of undertaking mineral processing.

Figure 22. W-tailings: picture after screening (@BRGM)

Smaller samples were then prepared using a manual two-ways splitter. **Table 14** summarizes samples provided by BRGM regarding W-tailings2 material among the project partners.

Table 14. W-tailings2: delivery of sub-samples to partners

W-tailings2	Dedicated for	Weight (kg)
AGQ	Chemical analysis	1
BRGM	Chemical analysis per size fraction	2

7.2.   Chemical composition

Figures of homogenised samples are discussed hereafter. MW sample is rich in Si (measured by pXRF but not analysed by ICP), with some Al, Fe, K and Ca. It contains 1857 ppm W. Other targeted CRM are: 6 ppm Co, 7 ppm Sb, Ge being below detection limits (<10). Precious metals analyses give: 0.2 ppm Au and 6 ppm Ag.

7.3.   Particle size distribution

Table 15. W-tailings: particle size distribution (wet); Fe. Al. Cu. Pb. and W contents (pXRF)

Particle size	Distribution	Fe	Al	Cu	Pb	W
µm	% mass	%mass	%mass	ppm	ppm	ppm
>1000	5.7	6.1	2.8	381	17	6612
500-1000	24.5	5.7	2.4	482	59	5361
250-500	24.9	5.9	2.7	562	52	3614
100-250	19.4	65.6	2.7	745	60	1927
40-100	13.8	76.7	2.9	1494	103	3984
< 40	11.7	18.3	2.1	2452	579	8343

Particle size	Distribution	Fe	Al	Cu	Pb	W
Calculated (global)	100.0	7.4	2.6	916	122	4491

Wet sieving has been carried out on the product after crushed steps. The percentages of chemical elements in different size fractions of W-tailings sample are presented in Table 15.

First measurements by pXRF to compare size fractions show that Al and W are distributed in all size fractions. Fe, Cu show some variability, Cu and Pb being concentrated in the fine fraction (< 40 µm).

7.4. Other data

Mineral processing is on course on this sample to concentrate W-minerals. Results will be included in D1.2.

8. Results: Au-tailings

Two samples named Au-tailings 3 and 4 from Chile was selected by sample provider and analysed at first step of selection and including cyanides following information on the nature of the sample. Si was not analysed but should be main major elements related to quartz and silicate content. MW is carbonated (2 and 2.2 % C inorganic expressed as $CaCO_3$ are 16.6 and 18.3 %) with no sulfides. Targeted CRM are: 119 and 313 ppm Co. 20 and 16 ppm Sb. Ge and W being below detection limits (<10 and < 50 ppm). Precious metals analyses give: 0.4 and 2.5 ppm Au and 18 ppm Ag (one sample). CN total was 0.012 ppm in one sample and 383 ppm in the richest in Au.

A report was also prepared on the Chilean context of mine and tailings that we be further exploited in other WPs in the coming months.

9. Conclusion

Several MW containing some base metals, CRM and precious metals have been selected within RAWMINA consortium, sampled by 4 sample providers (1 kg then 1 big-bag), characterised and prepared to provide homogenised sub-samples for further work in WP2 on representative samples.

Mineral processing is currently undertaken on W-tailings and results will be described on D1.2.