Characterization of ancient mine wastes: an approach for environmental management and metals recovery

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ERA-MIN NETWORK ON THE INDUSTRIAL HANDLING OF RAW MATERIALS FOR EUROPEAN INDUSTRIES

FCT Fundação para a Ciência e a Tecnologia MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

Introduction

INDUSTRIAL AND MINING WASTES - CHALLENGE FOR MANY COUNTRIES

ANCIENT MINE WASTES - THREAT OR AN OPPORTUNITY ?

THREAT:

Simply abandoned and measures are not are not taken to reduce the risks to the environment;

OPPORTUNITY:

Resource of critical and valuable metals with potential economic benefits.

Deposits of mine wastes – reflect low efficient extraction methods from past – often contain significant amounts of valuable metals.

Waste reprocessing reduce environmental liabilities.

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Introduction

MINING WASTE TREATMENT PROCESS - physical and chemical characteristics for reprocessing activities or environmental protection.

ENVIRONMENTAL IMPACTS - mitigation and/or remediation options - properties and behavior in the environment (geotechnical stability, release of dissolved metals, acidity or suspended particles serious and long-lasting problems).

CASE STUDY - Cabeço do Pião tailings impoundment - Interest in reprocessing coexists with the need to solve environmental problems due to instability of the unconfined tailings.

Objectives

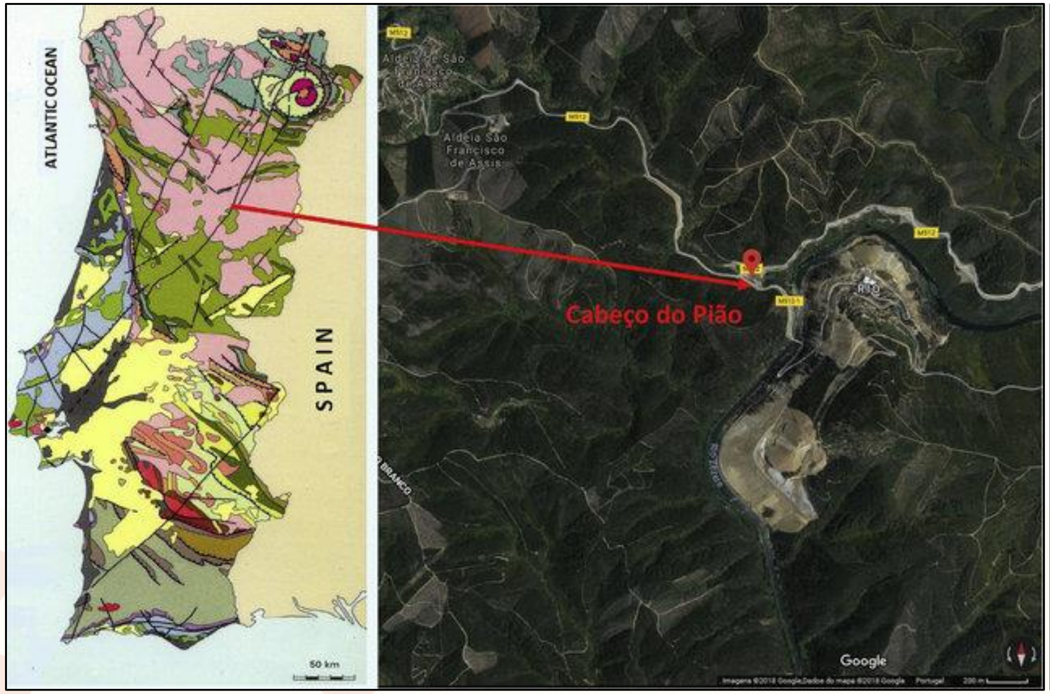
PURPOSE OF THE PRESENT STUDY

- Generate detailed characterization of a mine waste deposit to be able to identify potentially economic metals and mineral, select best extraction method and perform risk assessment.
- Strategy economic value by reprocessing ***vs*** feasible environmental wastes management approach.
- Sub-task of the ERA-MIN project ReMinE - **Improve Resource Efficiency and Minimize Environmental Footprint**, https://www.ltu.se/proj/Improve-Resource-Efficiency-and-Minimize-Environmental-Footprint-REMinE?l=en.

Methods and materials

STUDY AREA

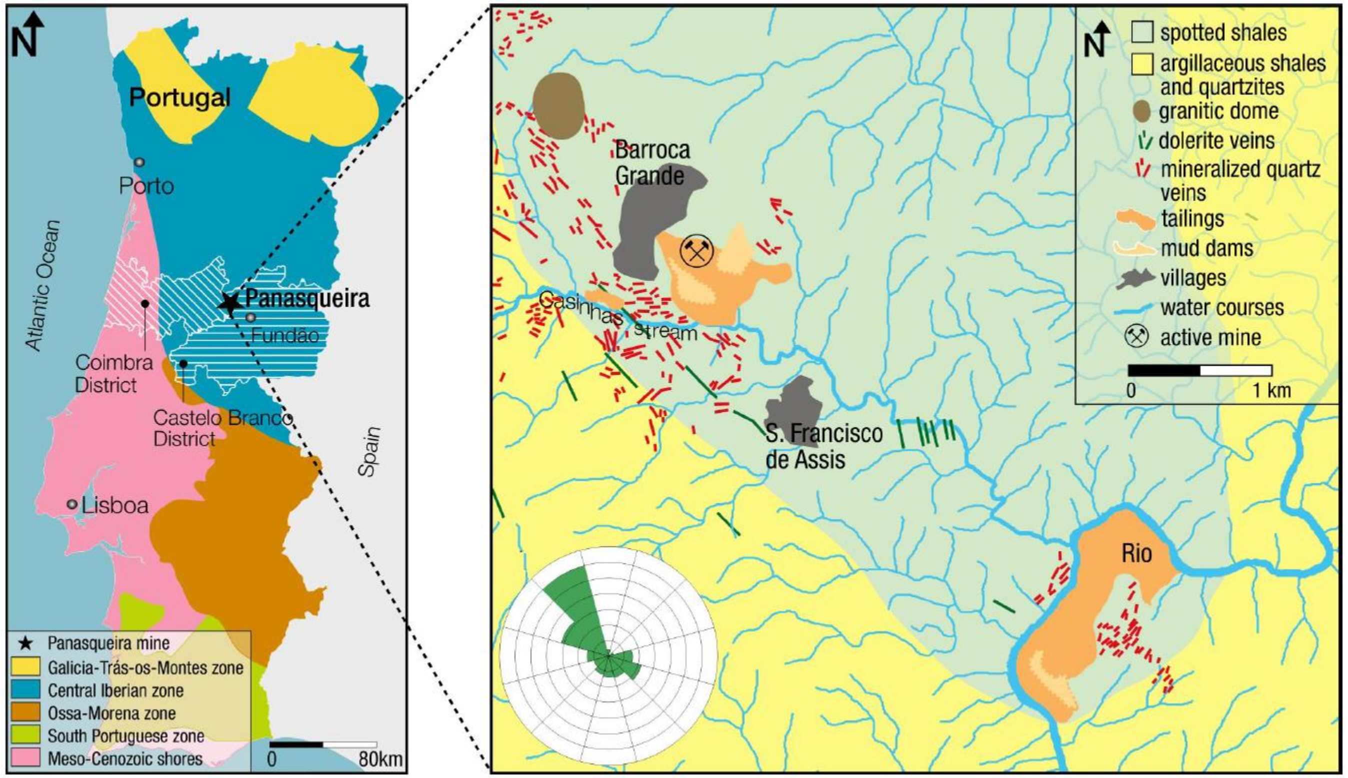
- Cabeço do Pião tailings impoundment belonged to Industrial Complex of Panasqueira mine - one of the largest operating tungsten mines in the Market Economy Countries (MEC).
- Mine started operating in 1896 - wolframite exploitation, cassiterite and chalcopyrite as by-products.



Methods and materials

STUDY AREA

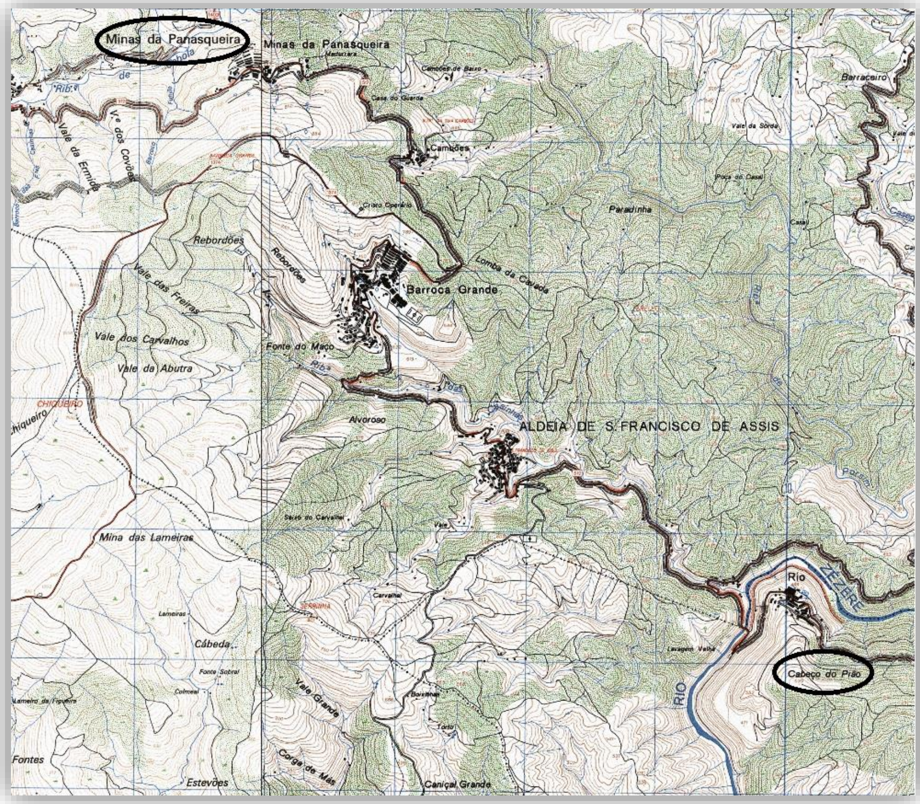
- Cabeço do Pião - W ore was processed in a large scale.
- Main processing plant later moved to the Panasqueira village, treating ores from several orebodies in the area.



Methods and materials

STUDY AREA

- Tailings at Cabeço do Pião site impoundment around a hill on the edge of the Zêzere River (1927 and for 90 years).
- Slope of the crest and supporting bedrock is 35°, h ≅ 90 m, draining directly to the Zêzere River.



Cabeço do Pião (W.S. location)

Methods and materials

STUDY AREA - TAILINGS

- V = 1.32 x 10^6 m^3
- Exposed to atmospheric conditions, altered by chemical, mineralogical, physical and geotechnical factors.

STUDY AREA - ARSENOPYRITE STOCKPILE

- V = 9400 m^3 deposited near former processing plant - exposed until 2006, capped with geotextile and layers of clay.

STUDY AREA – LOCAL CONDITIONS

- Altitude 350 - 1080 m forming deep valleys.
- Zêzere River - main watercourse in the area.
- Climatic conditions can be extreme – rainy, windy winters and very dry, hot summers.
- Precipitation - 1600 mm/year, frequently snows events above altitude of 700 m.
- Average temperature 0º C (winter) - 30º C (summer).

Methods and materials

STUDY AREA - TAILINGS SAMPLING

- Sampling events November 2016 and January 2017.
- Rectangular grid of 40 x 20 m.
- 41 surface samples (50 to 60 cm depth) - relevant for wind transport, exposure and direct contact with precipitation and surface runoff – “S”.
- 41 deep samples (≅ 2 m) – “P”.
- Samples identified from A to F followed by a numbering sequence from the right to the left side of the figure.

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Methods and materials

SOURCE CHARACTERIZATION - METHODOLOGY

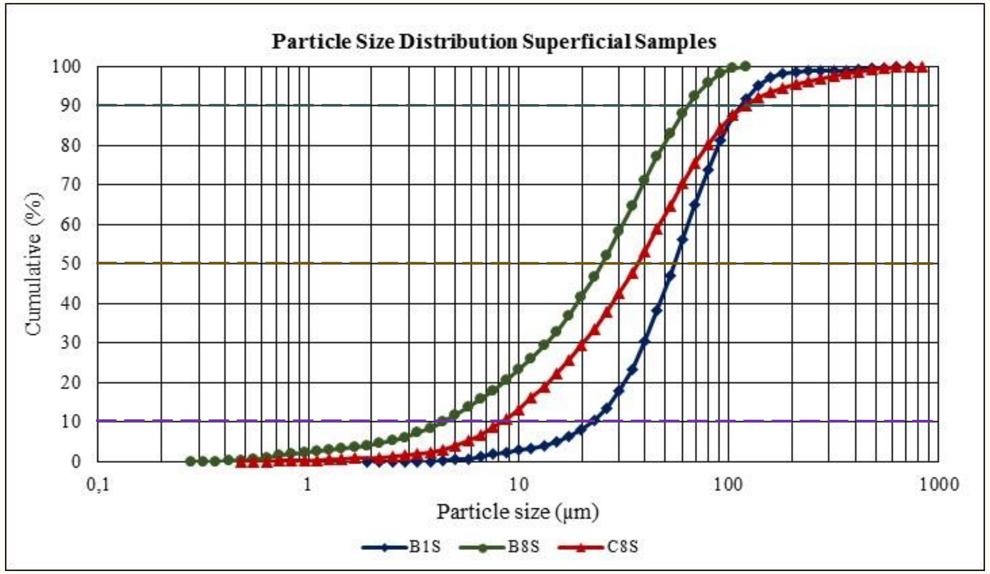
1. **Sampling and collection tailings samples**
   - Selection of tailings samples from Cabeço do Pião tailings disposal.
2. **Characterization of tailings samples**
   - Particle size distribution.
   - Chemical composition (main heavy metals).
   - Environmental properties: tailings pH.
   - Physical parameters: bulk density, particles density and voids %.
3. **Leaching tests**
   - Natural leaching test: pH, Salinity, EC, Eh, DO, BOD, etc.
4. **Forecast acid generation tests**
   - Different Acid Generation (AMD) prediction tests: NAG and ABA.

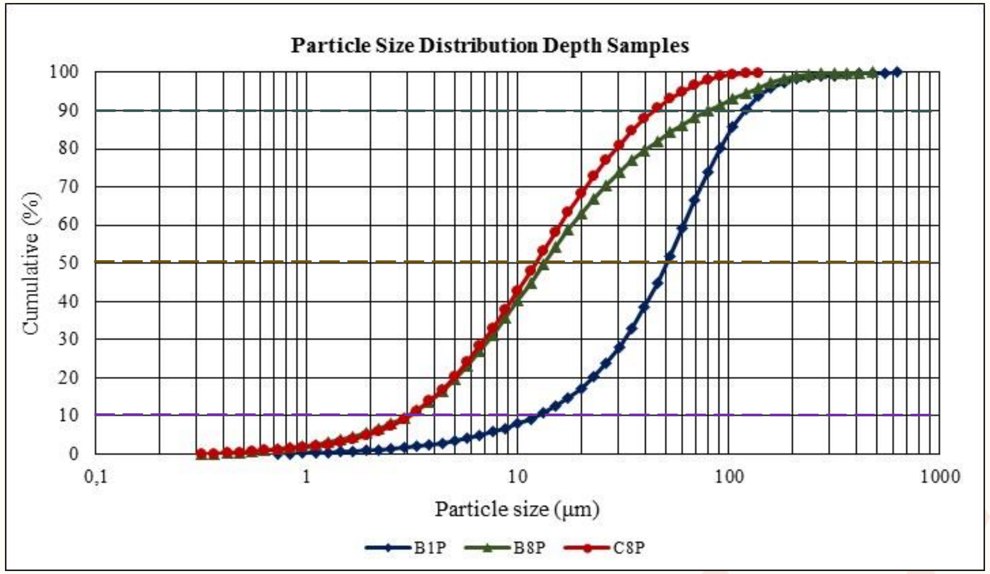
Results and discussion

RESULTS - PARTICLE SIZE DISTRIBUTION

- Heterogeneous samples - grain size;
  - ✓ “S” samples: 0.25 - 900 µm;
  - ✓ “P” samples: 0.30 - 700 µm;
  - ✓ Silt-sized particles (4 - 62 µm) – highest content;
  - ✓ Sand-sized particles (62 - 1000 µm);
  - ✓ Clay-sized particles (< 4 µm) – lowest content.

Composition	B1S	B1P	B8S	B8P	C8S	C8P
Sand content (%)	34	41	8	16	24	7
Silt content (%)	65	57	84	73	73	82
Clay content (%)	1	2	8	11	3	11
D10: 10% < µm	22	13	4	3	8	3
D50: 50% < µm	55	50	25	13	35	12
D90: 90% <µm	100	102	70	80	100	46





Results and discussion

RESULTS - PARTICLE SIZE DISTRIBUTION:

- Tendency of **sand fraction to increase** and **silt fraction to decrease** with depth **arise from**:
  - ✓ Preferred sedimentation of the coarse sand particles upon disposal of the slurry.
  - ✓ Oxidation and weathering of tailings surface would cause a significant decrease of the grain size with depth.

- Some **surface samples present coarser grain size than deeper samples,** high grain size variations:
  - ✓ Variations related to the distance from the tailings discharge pipe where the tailings were discharged as slurry;
    - ✓ Coarser grains settled closer to the pipe, while the finer grains settled further away.
  - ✓ Redeposited tailings in some areas of the impoundment.

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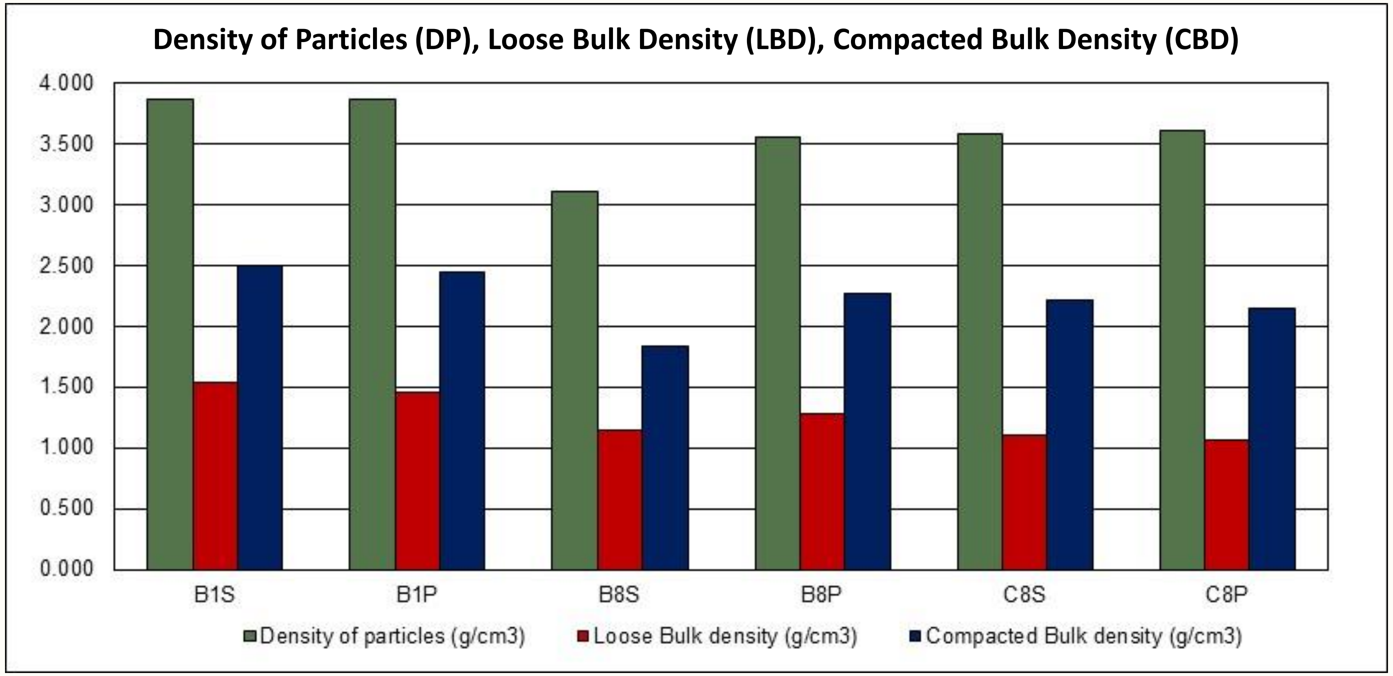
Results and discussion

RESULTS – DENSITY AND VOIDS %:

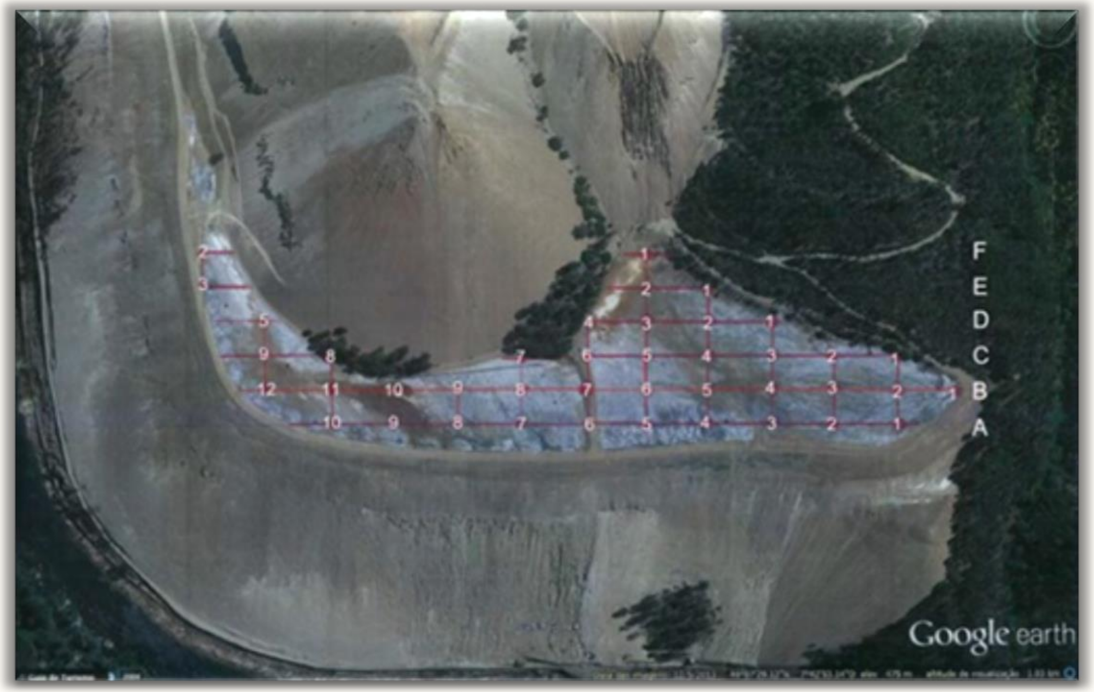
Sample ID	DP (g/cm^3)	LBD (g/cm^3)	CBD (g/cm^3)	VD (%)
B1S	3.86	1.54	2.50	35-60
B1P	3.86	1.46	2.44	38-62
B8S	3.11	1.14	1.83	41-63
B8P	3.56	1.28	2.27	37-64
C8S	3.58	1.10	2.22	39-69
C8P	3.61	1.07	2.14	41-70



Results and discussion

RESULTS – DENSITY AND VOIDS %:

Tailings ID samples	DP (g/cm^3)	LBD (g/cm^3)	CBD (g/cm^3)	VD (%)
"S"	3.16 - 3.76	1.10 - 1.54	1.83 - 2.50	35 - 41%
"P"	3.58 - 3.89	1.07 - 1.46	2.14 - 2.44	37 - 41%



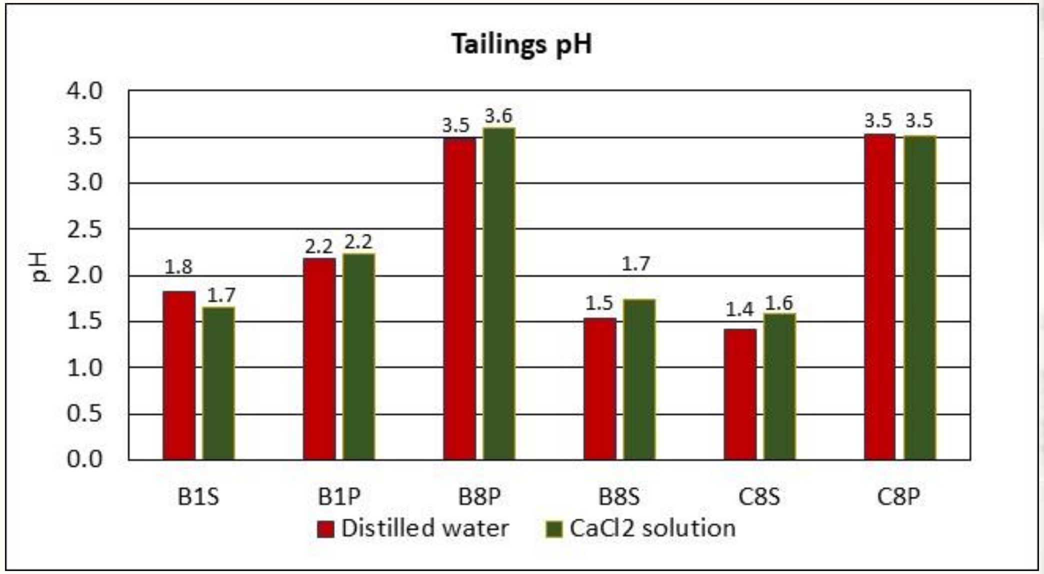
- ✓ Low bulk densities;
- ✓ No significant variation with depth;
- ✓ Voids % slightly decreased for deeper samples evidencing some consolidation (few cases).

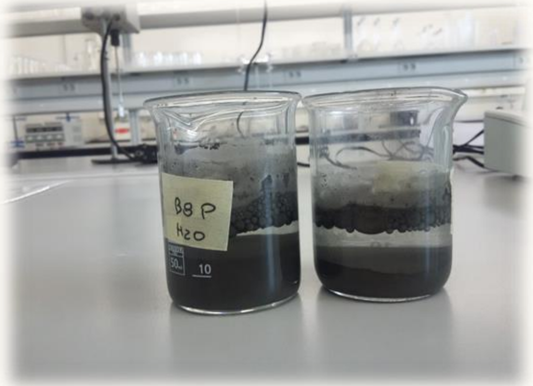
<u>An effective porosity of the tailings in depth will limit the infiltration of water and oxygen</u>.

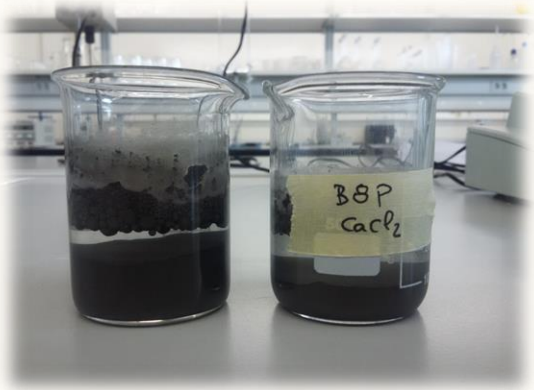
Results and discussion

RESULTS – TAILINGS SAMPLES pH:

Tailings pH determination (1.4 - 3.60)		
Sample ID	Distilled water	$CaCl_2$ solution
	pH	pH
B1S	1.8	1.7
B1P	2.2	2.2
B8S	1.5	1.7
B8P	3.5	3.6
C8S	1.4	1.6
C8P	3.5	3.5







- "S" samples - lower pH than "P" samples - atmospheric oxidation of the exposed pyrite minerals in the surface.

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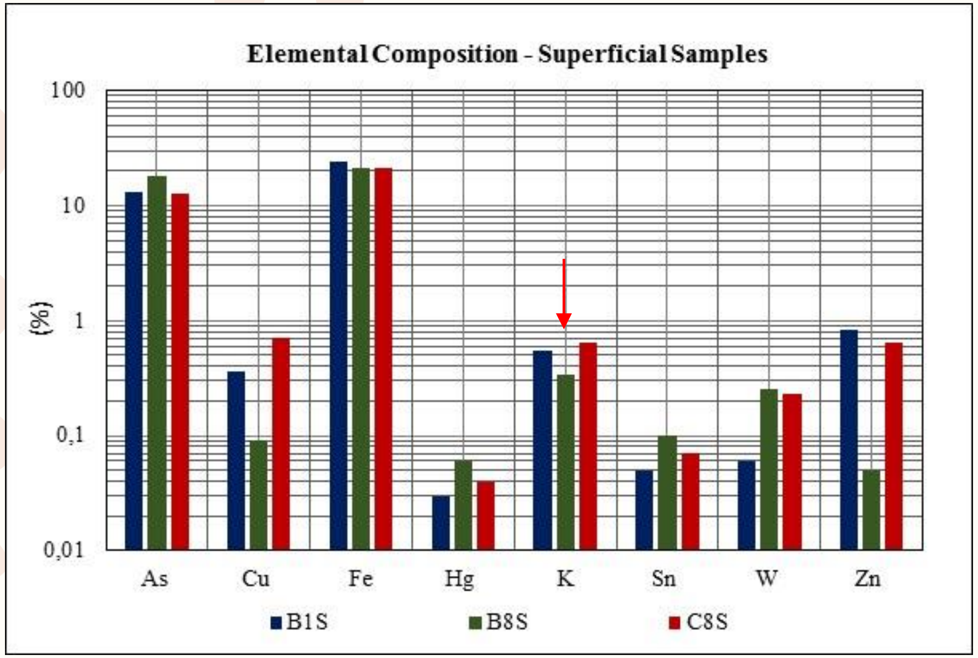
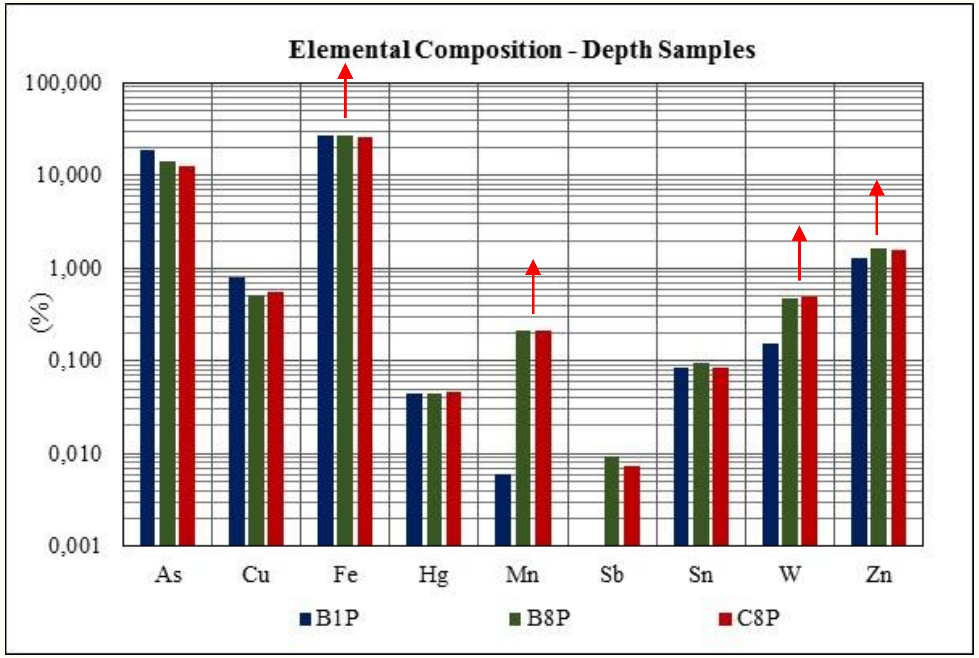
Results and discussion

RESULTS – CHEMICAL COMPOSITION:





- Prevalence of Fe (≅ 25 %) and As (12-20 %), followed by Zn (0.99 %), Cu (0.5 %) and W (0.28 %).
- **As** increases with depth for B1 and B8; decreases for C8.
- Environmental concern - **high As content:** oxidation of sulfide minerals + water = acidic mine drainage.

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Results and discussion

RESULTS – ELEMENTAL COMPOSITION:

- Previous studies - **As enriched from the surface down to a depth of 13 m**, concentration 9 - 24%.
  - From here, As decreases to values near or below 1%.
- X-ray diffraction - quartz, mica, feldspar, ilite-vermiculite, arsenopyrite, marcasite, pyrite, pyrrhotite and chalcopyrite.
- Others minerals - scorodite and natrojarosite present - **enriched in As, Cu, Mn, Pb and Zn**.
- **Fine-grained materials, high As content:**
  - Most immediate environmental concerns - **potential transport**, **dispersion by wind and proximity to Zêzere River**.
  - Other elements at high concentration in particles - **readily mobilized** during ongoing removal and processing.
- Material from the **arsenopyrite stockpile deposited on the top of the tailings**:
  - High Ag (124 mg/kg), As (210,000 mg/kg), Cd (3057 mg/kg), Cu (1426 mg/kg), Fe (19.8%), W (5166 mg/kg) and Zn (460 mg/kg).

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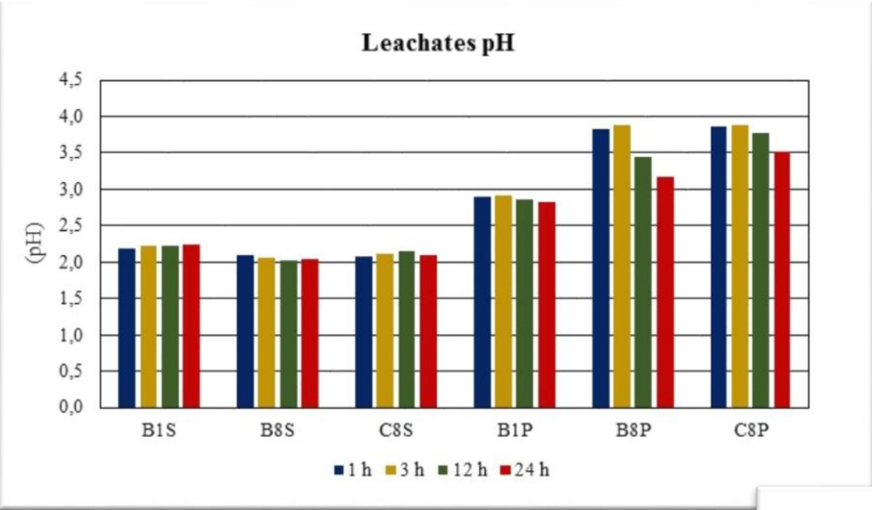
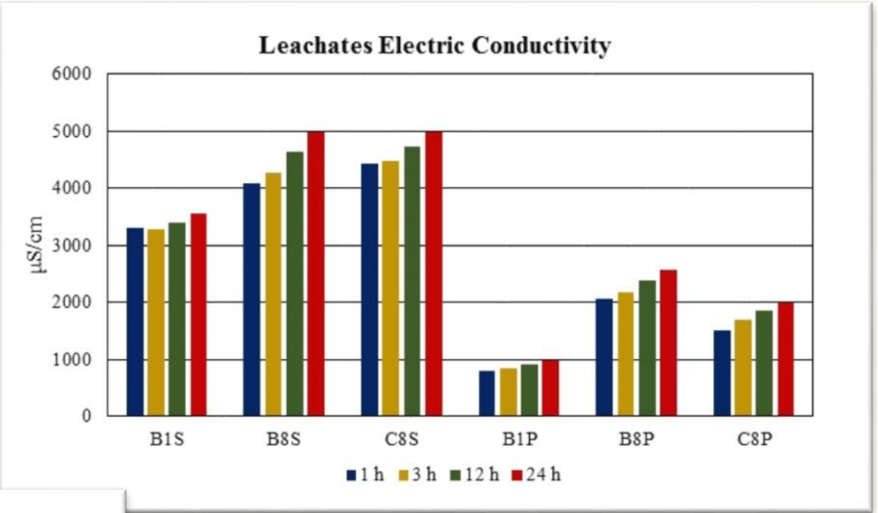
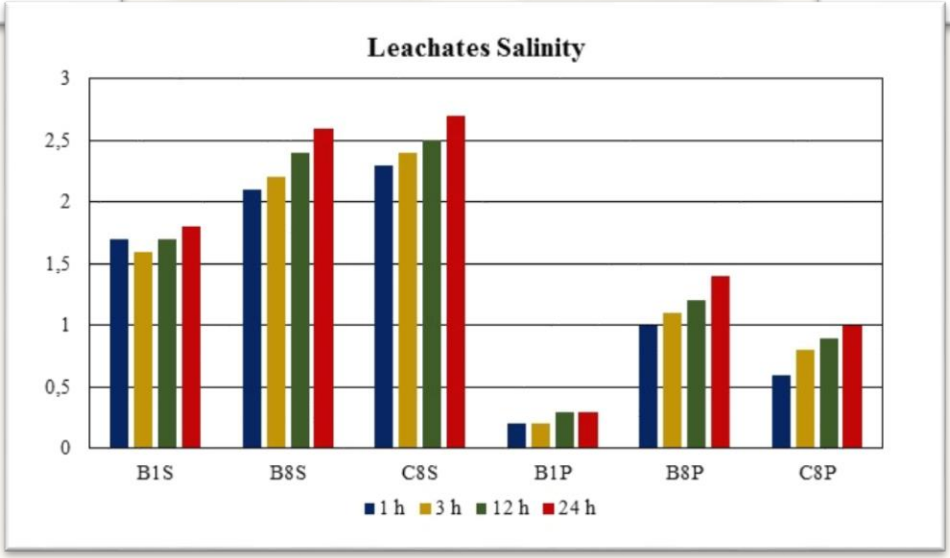
Results and discussion

RESULTS – NATURAL LEACHING TESTS - Variation of leachate characteristics over time: pH, SAL, EC







pH:

✓ Water leaching solution significant decrease to similar pH values of the collected samples:

"S" samples - pH (t_0) ≅ 6.5; pH (t_{24}) ≅ 2.0

"P" samples - pH (t_0) ≅ 7.2; pH (t_{24}) ≅ 2.3

Salinity and EC:

✓ Both increase, higher for "S" samples (more oxidizing environment).

EC and SAL increase; pH decrease:

✓ Indicate oxidation activity.

Results and discussion

RESULTS – NATURAL LEACHING TESTS:

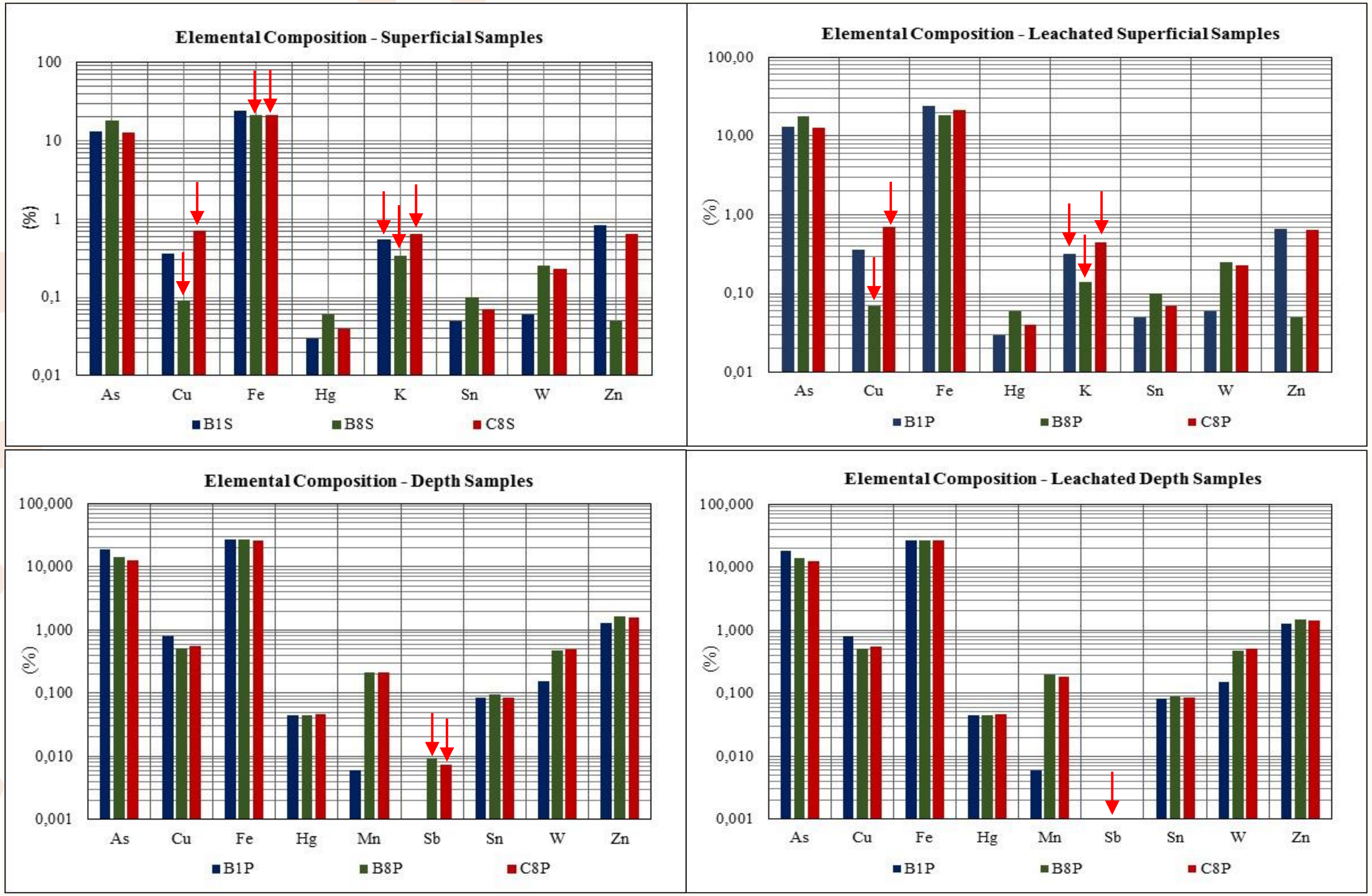
- Typical pH values of impacted waters - weathering sulphide minerals in the tailings.
- Occurrence of acid drainage - base of the tailings embankment - consequent iron coating and ferruginous crust.
- Chemical composition - high concentrations of dissolved sulfates, Al, As, Cd, Co, Cu, Fe, Mn, Ni, and Zn - indicative oxidation and dissolution of sulphides (pyrite, chalcopyrite, sphalerite and arsenopyrite).
- pH < 5 - potential aquatic toxicity from cationic metals (Al, Cd, Cu, Ni, Pb an Zn).

seepage collection channel on the base of the deposit

AMD draining directly to the river

Results and discussion

RESULTS – NATURAL LEACHING TESTS - COMPOSITION OF THE SOLID RESIDUE AFTER NATURAL LEACHING TEST



- ✓ Same before/after leaching tests;
  - ✓ Few exceptions: Cu, Fe, K, Zn.
- ✓ Although leachate acidic pH; EC, SAL increase over time: high concentrations of dissolved sulphates and metals:
  - ✓ Limit effect of AMD - iron oxides efficiently fixate some contaminants (As).
  - ✓ Oxidation of sulphide minerals of the uncovered mine tailings contact with water.

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Results and discussion

RESULTS – NET ACID GENERATION METHOD (NAG):

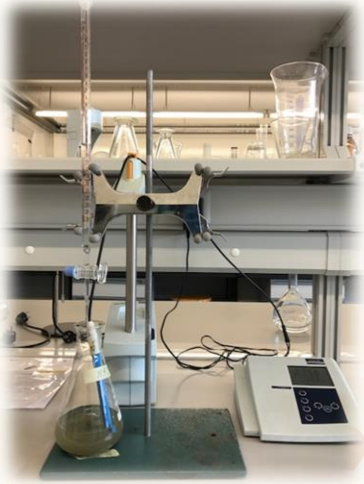
Determine total acid generating.

High risk of acid generating: “Potentially Acid Forming” (PAF) - Geochemical Classification Criteria, NAG value and NAG pH.

Sample	NAG pH	NAG values (kg H_2SO_4/t)
B1S	2.12	58.21
B1P	2.22	44.69
B8S	1.98	91.14
B8P	2.32	54.88
C8S	2.10	61.94
C8P	2.24	52.14

Likely to be acid drainage source “PAF”

pH | ≃ 2



pH | 4.5

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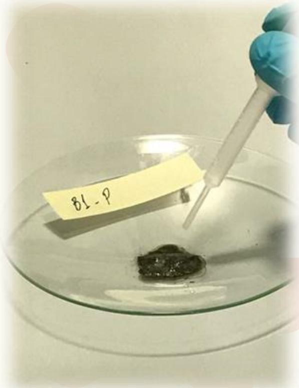
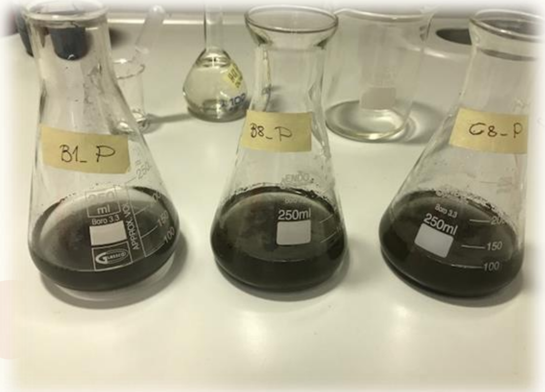
Results and discussion

RESULTS – ACID BASE ACCOUNTING NEUTRALIZING CAPACITY (MODIFIED ABA):



“Fizz” test



“Wide mouth conical flask”

pH	≅ 2

Net NP <-20 (kg $CaCO_3$/t) likely to form acid

Sample	pH	NP (kg $CaCO_3$/t)	AP (kg $CaCO_3$/t)	Net NP (kg $CaCO_3$/t)
B1S	8.51	-53.25	3.08	-56.33
B1P	8.40	-31.95	3.25	-34.75
B8S	8.36	-57.00	0.77	-57.77
B8P	8.30	-50.90	2.33	-52.33
C8S	8.33	-52.00	3.14	-55.14
C8P	8.34	-52.15	2.34	-53.59

Likely to be an acid drainage source: “PAF”

✓Individually, each test has limitations in how accurately it can predict AP and NP - good practice to use a combination of methods.

✓ABA method results, along with NAG results - these samples produce acidity (PAF) - tailings are a source of acidity generated under natural oxidation processes.

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Results and discussion

Reprocessing Investigations and Environmental Alternatives:

- Tailings reprocessing could represent a promising source of zinc ores:
  - Zinc ores can be concentrated by acidic leaching - disadvantage of dissolving other elements: Fe, Ca, Mg and Si.
  - Several leaching tests were already performed with sulfuric acid and hydrochloric acid-oxygen leaching:
    - Zinc concentration process was limited by the content of Fe and As in samples material.
    - Leaching tests were more effective when performed with sulfuric acid but the recovery was only up to 50%.
- Alkaline extraction tests are ongoing.

Results and discussion

Reprocessing Investigations and Environmental Alternatives:

- **Issues from reprocessing process:**

  i. Low tonnage of W, Cu and Zn content in the tailings, high capital costs and foreseen high processing costs.

  ii. Uncertainty remains about **As** problem and if it will be solved with reprocessing.

- **Alternatives to minimize environmental impacts may include:**

  i. Cover the tailings on-site, avoiding leaching and weathering:

  ✓ Topographical issues imply a complete reshape of the disposal and large movement of ground in a difficult topography.

  ii. Excavation and transport of the tailings to other location for final confinement:

  ✓ Main advantage - effective possibility of sealing the tailings;

  ✓ Large volume to be transported, reshape and selection of a new site to deposit the tailings.

Results and discussion

Reprocessing Investigations and Environmental Alternatives:

iii. Ex-situ inertization

- ✓ Main advantage - inertization of the tailings - several solutions - cementation, solidification and polymeric resins.
- ✓ Disadvantage - excavation of the tailings and transport to a new location also, costs.

iv. In-situ inertization

- ✓ Main advantage avoid transport.
- ✓ However, the feasibility of this alternative is not certain - several possible variations: cement, clays, polymeric resins, geochemical immobilization.

Conclusions

- Tailings characterization: particle size, elemental composition, leaching behaviour and potential for acid production.

- Results analysed through two different approaches based on the economic and environmental assessment of the two main alternatives, reprocessing or removal.

  - ✓ High As content along with the fine-grained nature of the materials - most immediate environmental concerns.

  - ✓ Acid generation forecast test - tailings samples as “potentially acid forming”.

  - ✓ High grades in W, Cu and Zn - possibility for profitable reprocessing of the tailings.

Conclusions

- Several alternatives considered for the Cabeço do Pião tailings deposit, but not without some drawbacks.
  - ✓ Reprocessing the tailings - low tonnage of valuable metals in the tailings;
  - ✓ And cost of the recovery process are the main constraints.
- Environmental solutions - all alternatives have advantages and disadvantages but the ones avoiding excavation and transport will be preferable.
- After tailings characterization and reprocessing optimization - go through a decision-making process, determining the pros and cons of each alternative and perform a cost-benefit analysis for each alternative.

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Acknowledgments

This work is part of the project REMinE that was funded with public national funds from FCT under the programme for International Cooperation ERA-NET, supported by ERA-MIN (2011-2015) funded under the EU 7th Framework Programme FP7-NMP.

Thank You!

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