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# A Holistic Approach in Re-Mining Old Tailings Deposits for the Supply of Critical-Metals: A Portuguese Case Study

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Received: 31 July 2019; Accepted: 12 October 2019; Published: 17 October 2019



**Abstract:** Demand growth for metallic minerals has been faced with the need for new techniques and improving technologies for all mining life-cycle operations. Nowadays, the exploitation of old tailings and mine-waste facilities could be a solution to this demand, with economic and environmental advantages. The Panasqueira Mine has been operating for more than a century, extracting tungsten and tin ore. Its first processing plant, “Rio”, was located near the Zêrere river, where mineral-processing residues were deposited on the top hillside on the margin of this river in the Cabeço do Pião tailings dam. The lack of maintenance and monitoring of this enormous structure in the last twenty years represents a high risk to the environment and the population of the surrounding region. A field-sample campaign allowed the collection of data, and resulted from laboratory tests to use regression optimization. Re-mining the tailings by hydrometallurgical methods was considered to satisfy the two conditions of metal demand and environmental risk. The metal content in Cabeço do Pião was shown to be enough for environmental restoration. The re-mining solution was studied, taking into account the technical, economic, social, and environmental aspects.

**Keywords:** tungsten; zinc; tailings reprocessing; modeling regression; surface response

## 1. Introduction

Over many years of mineral exploitation, millions of tons of mining waste and tailings were deposited, often incorrectly, into the environment. Technology that was available decades ago and the lack of environmental control are factors that contributed to this indiscriminate disposal. However, tailings may be a source of high-grade minerals and supply metals with substantial economic value in the current mineral market. They could also be used as raw material in the production of concrete composites [1,2]. As the remaining metals contained in the solid phase of tailings, not recovered at the time of production, represent potential resources, reprocessing could be an alternative to global metal consumption from the perspective of sustainable mining [3–5].

Tailings dams are part of the legacy left by an intensive mining industry and are frequently associated with environmental damage, social impact, and a possible failure of dam structures. A holistic approach with a complete overview of the technical, environmental, social, and economic aspects could be effective in the assessment of a re-mining project for all affected stakeholders. The European project ERA-MIN REMinE: Improve Resource Efficiency and Minimize Environmental Footprint was developed by institutions from three countries, Portugal, Romania, and Sweden, which have a long

history of mining in the last century. Its scope, which includes assessment of sustainable alternatives to tailings dams in these countries, as well the reprocessing of tailings, was studied [6,7].

The Cabeço do Pião dam, presently owned by the municipality of Fundão, a Portuguese case study, has stored mining waste and tailings from processing plant Rio that was part of the Panasqueira Mine Complex. Cabeço do Pião is in the countryside, in a location with several villages dispersed between mountains (Figure 1).



**Figure 1.** Cabeço do Pião dam location in Portugal and surrounding villages. Map data: Google Earth Pro, Maxar Technologies [8].

The Panasqueira Mine, in operation for more than 100 years, consists of a deposit of hydrothermal quartz–wolframite veins intruding into schists, known as Beira schists, and shales [9], where cassiterite and chalcopyrite were ore minerals associated with arsenopyrite and pyrite.

Materials, stored in the dam for more than fifty years, with harmful elements such as arsenic, cadmium, copper, and zinc, are a liability to the environment, the surrounding region, and the local population. Cabeço do Pião has a large volume of roughly 1,900,000 m<sup>3</sup>, with an average height of 90 m and a steep slope gradient of up to 35° at the Zêzere riverside. However, materials that are interesting for recovery are fine tailings produced during an antiquated process of recovering wolframite, with a total of 731,034 m<sup>3</sup> of the volume discharged at the top of the dam.

Many research methodologies were applied to study the abandoned mine site aiming to understand the properties and behavior of the tailings in the environment, such as geochemical analysis from different sampling media and the relationship of leaching, transport, and the accumulation of some heavy metals from the tailings to the environment [10]; and analysis of the potential risk of contamination in the soil or through human contact [11].

The main aim of this work was to show the tailings re-mining progress, a highly complex and ambitious project involving different aspects: the technical, economic, social, and environmental.

## 2. Materials and Methods

In this study, an integrated assessment of the reprocessing project is proposed as a holistic approach to commit with economic goals, environmental constraints, social development, and technical feasibility. From the perspective of sustainable re-mining activities, the following methodology was applied to support decision-makers for the execution of the project.

## 2.1. Field Research

### 2.1.1. Social Survey

A social survey was developed and applied to obtain the quantitative data of socioeconomic characteristics of residents near the Cabeço do Pião dam. Surveys, interviews, and meetings with the local community also aimed to seek understanding between stakeholders and to obtain a social operation license. The survey consisted of objective questions that included requesting information about the socioeconomic and health conditions of the interviewee's family. It comprised questions regarding the perception of the risks and damage associated with the Cabeço do Pião dam, as well as expectations regarding the solution of the problem.

The small population of these villages work in agriculture, mining, and other activities resulting from it. The population for this research were the residents of the village of Cabeço do Pião, of villages up- and downstream from the dam, and residents of the Fundão Municipality (the current owner for the facilities of Cabeço do Pião). Villages, total population, total area, population density, and distance from each village to the dam are shown in Table 1.

**Table 1.** Population distribution in the Cabeço Pião <sup>1</sup> region.

Locality	Resident Population	Area (km <sup>2</sup> )	Population Density	Distance (km)
Fundão (Municipality)	29,213	700.2	41.7	25.7
Casegas e Ourundo (Villages)	797	48.25	16.5	10.7
Silvares (Village)	968	20.3	47.8	5.6
Barroca (Village)	496	23.1	21.5	10.3
Dornelas do Zêrere (Village)	682	16.44	41.5	13

<sup>1</sup> DGT-CAOP 2016, CENSOS 2011 [12,13].

Part of the population of this region has no real existence, that is, it is hypothetical or difficult to find. Therefore, a nonprobabilistic survey was considered, with interviewees randomly selected. However, a minimum 10% of the residents were intended to be interviewed as a target population, (294 people in total) to reach a statistically significant survey.

### 2.1.2. Sampling

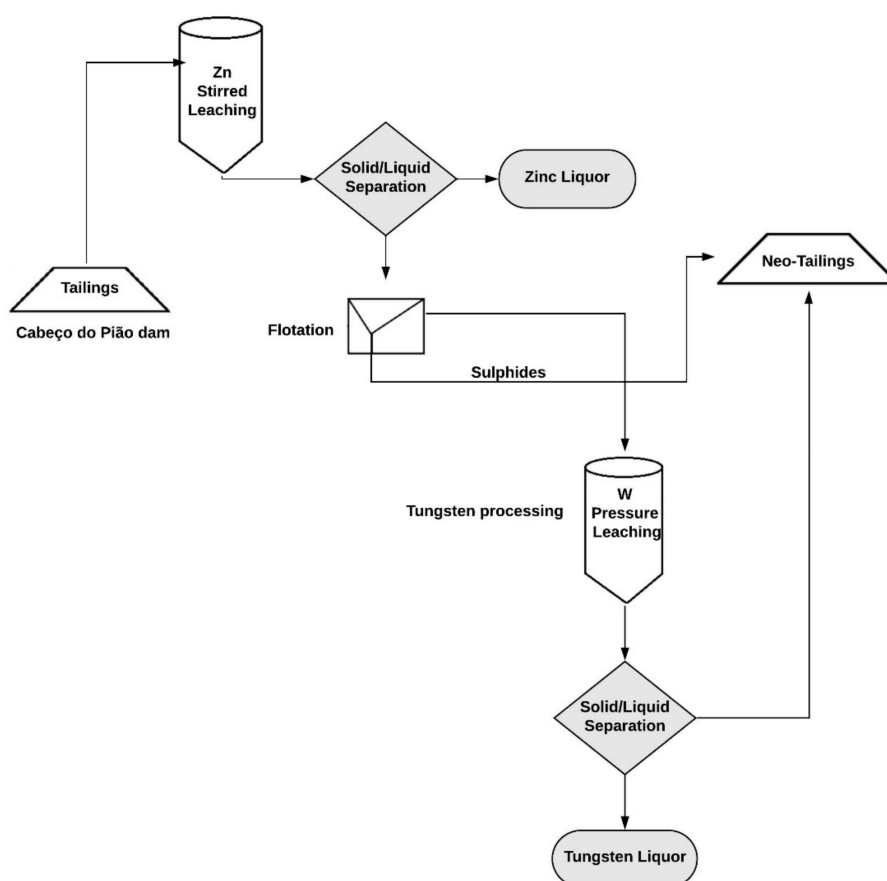
The tailings sampling campaign was conducted at the surface of the Cabeço do Pião area through a regular rectangular mesh grid of approximately 40 by 20 m. The sampled area was about 2.6 ha, with a total of 33 demarcated points. Their coordinates were determined by global position system (GPS) and georeferenced by a Universal Transverse Mercator (UTM) system. Sampling collection was performed at 2 different depths, 0.5 and 2.5 m, totaling 66 samples.

These 66 tailings samples were submitted for chemical analysis (energy dispersive X-ray fluorescence (XRF)) to determine the contents of the main elements in the tailings. Physical characterization was done according to the methodology described in [14], in which the particles under 200 mesh were submitted to particle-size analysis via laser diffraction, covered by ISO13320 (2009) using a Mastersize 2000 Ver. 5.60 (Malvern Instruments Ltd.).

In another stage of the project, 2 campaigns were carried out to collect leachates from the baseline of the dam, near the river, in March and June 2018; these leachates were chemically characterized.

## 2.2. Experiment Research

A conceptual flowsheet for the reprocessing plant was proposed by Figueiredo et al. [15] based on the preliminary results of chemical analysis, the researchers' experience, and the available information. The simplified flowsheet consisted of two small modular circuits (Figure 2).



**Figure 2.** Simplified reprocessing flowsheet proposed for the re-mining project of Cabeço do Pião.

As shown in Figure 2, a circuit was included to recover zinc in a stirred-tank reactor and for subsequent solid/liquid separation to obtain zinc liquor; another circuit to recover tungsten through primordial reverse flotation stage was included to eliminate sulfides in the froth. The physical–chemical tungsten processing is done through pressure leaching to obtain the tungsten liquor. Residues from both modular circuits are deposited in the neo-tailings storage facility.

The stages of the reprocessing plant, stirred-tank reactor, flotation, and pressure leach, were technically tested and evaluated through a methodology to adjust the experiment data in multiple regression models. Then, by analysis of the contour plots, we identified the optimal results as an assessment of the project feasibility.

### 2.2.1. Stirred-Tank Reactor Tests

The stirred-tank reactor tests were performed in a reactor with a volume of 0.5 L. The average agitation speed of the solution was 225 rpm, with 0.1667 kg sample mass. Samples were composed of a blend of 2 original samples from Cabeço do Pião tailings, selected according to the highest zinc content. Leaching tests were performed with a solid ratio of between 10% and 40% (w/v), in acid medium, in a total solution of 0.25 L, prepared using sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and ferric sulfate ( $\text{Fe}(\text{SO}_4)_3$ ,  $0.5 \text{ mol}\cdot\text{L}^{-1}$ ) as a reagent.

For each test, 0.02 L of the representative leach-liquor sample was taken from the reactor after 1, 2, 4 h, and at the end of tests at 6 h. All the liquid-leaching samples were filtered, the solid residues were analyzed with XRF, and the liquors were analyzed by flame atomic absorption spectroscopy [16].

The solid ratio, temperature, and sulfuric acid concentration varied in each experiment; ferric sulfate concentration and leaching time were kept constant in all 9 tests. The objective of the leaching in the stirred-tank reactor was to extract zinc from the tailings into a soluble liquor.

### 2.2.2. Flotation Tests

Flotation tests were performed by a reverse route: roughing and scavenging under fixed batch conditions, with pH adjusted to 4; the chosen collector was MAXGOLD. Sample mass was approximately 1 kg from the Cabeço do Pião tailings blend, with a solid ratio of 30% (w/v). Air-flow rate at the roughing stage was 8 L·min<sup>-1</sup>, and 10 L·min<sup>-1</sup> at the scavenging stage.

The collector dosage and froth bed height varied in each experiment; pH, solid ratio, and air-flow rate were kept constant. The objective of the flotation was to recover arsenic into the froth as an intermediate stage of the reprocessing project to reduce sulfides in the material to be sent to the pressure leaching.

### 2.2.3. Pressure-Leaching Tests

Pressure leaching was done in a high pressure–temperature reactor with 0.4 kg of the sample mass from the Cabeço do Pião tailings. This stage had sodium hydroxide (NaOH, 40 mol·L<sup>-1</sup>) as a chemical leaching reagent, the solid ratio was 50% (w/v), and speed rotation was 400 rpm. Parameters pH and Eh were measured. After the leaching test, the liquor was filtered, and the solid residue was analyzed via XRF.

From these tests, temperature, pressure, and residence time varied in each experiment. The objective of pressure leaching was to extract tungsten from the tailings into a soluble liquor.

## 2.3. Experiment-Data Analysis and Modeling

It is known that factorial designs are efficiently used to study the response of experimental conditions in many experiments [17]. When an experimental design is not possible, the data obtained from experimental research could also be treated by regression methods. In many engineering problems, there are 2 or more variables (factors:  $x_1, x_2, \dots, x_k$ ) that are related and affect system response (dependent variable:  $y$ ). The relationship between these variables could be fitted by a multiple linear regression model [18], described by:

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \dots + \beta_kx_k + \epsilon, \quad (1)$$

where  $\beta_0$  is the plane intercept,  $\beta_1, \beta_2$ , and  $\beta_k$  are regression coefficients, and  $\epsilon$  is a random error term.

In this study, in all experimental tests, factors were chosen by results previously obtained in preliminary tests and kinetic studies [15], and were not put into codified values. In the first phase of fitting a regression model, the Analysis ToolPak add-in from Excel software was used. During the second phase, the Minitab software was used as an experiment-data analysis tool.

Model fitting was performed using the least-squares method for estimating regression coefficients. It was assumed that the error term  $\epsilon$  had  $E(\epsilon) = 0$  and  $V(\epsilon) = \sigma^2$ , which allowed for the hypothesis-testing procedures. As analysis requisition, the regression statistical significance test is useful to determine a linear relationship between response variable  $y$  and variables  $x_1, x_2, \dots, x_k$ . Confidence interval  $(1-\alpha)$  was 95%, variance analysis for the model was tested by the F-test and p-value, and model inadequacy was assessed by a lack-of-fit F-test when it was possible. The hypothesis test was also used to adjust each regression coefficient ( $\beta_1, \beta_2, \dots, \beta_k$ ). There were unplanned experiments with regard to the coefficient of determination ( $R^2$ ) that could not measure data variability [18].

The F-values of tests are parameters for comparing variance with error variance, and they are the ratios of mean squares. Moreover, p-values are the probabilities of F-value statistics to be exceeded [17]. The lack-of-fit (LOF) test was used to evaluate the adequacy of the models when it was possible. It is worth mentioning that a variable is statistically significant when its p-value is smaller than the significance level and could be identified in a Pareto chart with standardized effects.

Model adequacy, also important, was checked by residual plot analysis, aiming to ensure that the fitted model was an adequate approximation to the true system, and to verify that least-squares regression was not violated [18].



Response surface methodology (RSM) is used when several variables influence the response, and it is necessary to optimize this response. In other words, RSM is used to determine the best operation conditions in a series of experiments to obtain an optimal response. Through the prediction and verification of optimization conditions, a three-dimensional surface map is used intuitively. A contour plot, which is the projection of the response surface map, was used for better visualization of the optimal condition of a series of experiments [17–20].

#### 2.4. Economic Conceptual Analysis

As an initial study phase, conceptual economic analysis was performed considering the parametric method of the O'Hara cost estimator. This method is used in mine cost estimation to predict capital and operating costs [21].

### 3. Results

#### 3.1. Social-Survey Inference

As expected, the inaccessibility of the population interfered in the reasonably achieved quantitative results. Many residents were not found in their houses, and some had reasons to refuse to answer the survey, such as lack of knowledge about the problem or having an association with the mining company. This was assumed that it could happen, as these were reasons why social assessment in the mining sector has been a challenge [22]. The social survey was not statistically significant; only 1% of the target population agreed to answer the questionnaire. Therefore, for this work, it was not possible to present a useful metric for the social criteria. Given this scenario, the few obtained results were treated qualitatively to obtain an overview of the problem, considering them as interviews.

Analysis of the interviews and conversations with the locals made it possible to understand the reality of those who live nearby. According to the interviews, the degraded landscape seemed familiar, and the Cabeço do Pião dam did not seem as being at risk of rupture, or water, soil, and dust contamination to the population of the visited villages. However, since the latest dam collapses occurred in Brazil, social opinion has been changed.

#### 3.2. Physical–Chemical Characterization

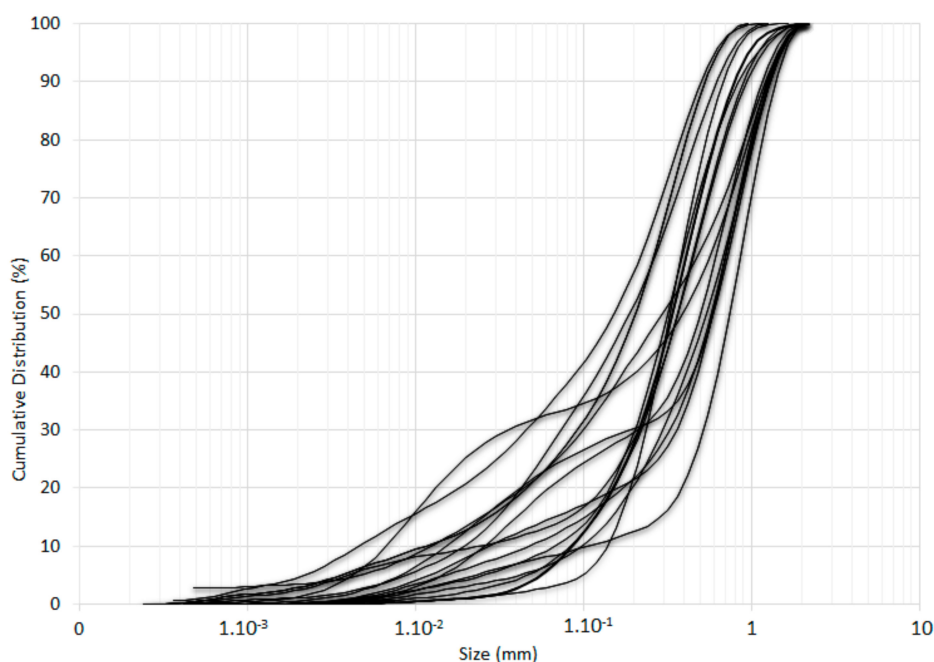
XRF analysis results on the content of the detected metals are shown in Table 2 [14], as well the descriptive statistics performed on the Microsoft Excel (2016)

**Table 2.** Descriptive statistics of chemical elements in tailings from Cabeço do Pião samples [14].

Element	Mean	Min.	Max.	Standard Error	Med.	Mode	Standard Deviation	Sample Variance
K	0.48	0.12	0.89	0.03	0.46	0.50	0.20	0.04
Ti	0.14	0.02	0.24	0.01	0.15	0.14	0.05	0.00
Mn	0.09	0.01	0.29	0.01	0.05	0.01	0.08	0.01
Fe	23.40	16.29	28.51	0.39	23.7	22.36	2.64	6.97
Cu	0.45	0.03	1.21	0.04	0.43	0.47	0.25	0.06
Zn	0.97	0.03	1.91	0.07	1.04	1.27	0.48	0.23
As	13.55	7.13	26.78	0.59	13.11	16.58	3.98	15.82
Se	0.01	0.00	0.03	0.00	0.01	0.01	0.01	0.00
Rb	0.01	0.00	0.03	0.00	0.01	0.01	0.01	0.00
Zr	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.00
Sn	0.07	0.04	0.15	0.00	0.07	0.07	0.02	0.00
W	0.17	0.03	0.42	0.02	0.11	0.08	0.13	0.02
Hg	0.04	0.02	0.1	0.00	0.03	0.03	0.01	0.00
Bi	0.02	0.00	0.06	0.00	0.02	0.02	0.01	0.00
Cd	0.02	0.00	0.02	0.00	0.02	0.02	0.01	0.00

Mean contents of the metals of interest in wt% were zinc (0.97%), arsenic (13.55%), and tungsten (0.17%).

Particle-size distributions of the tailings samples from Cabeço do Pião are shown in Figure 3.



**Figure 3.** Particle-size distributions of tailings samples from Cabeço do Pião dam.

Analysis from Figure 3 allowed to conclude that tailings materials had particle size smaller than 1 mm. Granulometric parameter D50 was 0.36 mm on average.

Chemical analysis results of the tailings leachate are shown in Table 3 [23].

**Table 3.** Tailings leachate concentrations from Cabeço do Pião dam [23] in comparison with admissible values in Portuguese legislation (Decret-Law n° 236/98, 1 August 1998) [24].

	Concentration (mg·L <sup>-1</sup> )					
	Al	As	Cd	Cu	Mn	Zn
March	1150	99	0.44	44	138	59
June	113	6.3	0.45	37	252	55
Emission-limit values	10	1.0	0.2	1.0	2.0	–

Analyzing the arsenic concentration in both periods, there was substantial divergence that could be explained by the different locations of the samples, the varied climatic conditions of the two seasons, or the high seasonal variability that is typical of tailings with sulfur content. These results were used in the quantitative environmental-risk analysis [23] that permitted to conclude that the Cabeço do Pião dam has been affected in all environmental compartments.

### 3.3. Regression Modeling

Tables 4–6 present the experiment conditions and responses of zinc extraction, arsenic recovery, and tungsten extraction obtained in the stirred-tank reactor, flotation, and pressure-leaching tests, respectively.

**Table 4.** Experiment conditions and responses of stirred-tank reactor tests.

Standard Order	Experiment Order	Independent Variables			Responses
		Solid Ratio (%) $x_{11}$	Temperature ( $^{\circ}$ C; $x_{12}$ )	H <sub>2</sub> SO <sub>4</sub> (mol·L <sup>-1</sup> ; $x_{13}$ )	Zn Extraction (%)
1	1	0.4	80	0.5	51.42
2	2	0.4	80	0.5	55.77
3	4	0.4	50	0.5	20.33
4	5	0.4	20	0.5	10.03
5	3	0.4	80	0.5	46.34
6	6	0.2	80	0.5	55.56
7	7	0.1	80	0.5	54.23
8	8	0.4	80	0.75	48.46
9	9	0.4	80	0.25	34.52

**Table 5.** Experiment conditions and responses of flotation tests.

Experiment Order	Independent Variables		Responses
	Froth Bed Height (m)	Collector Dosage (g·t <sup>-1</sup> )	As Recovery (%)
1	3	45	61.88
2	6	45	45.37
3	3	67.5	45.20
4	6	67.5	58.27

**Table 6.** Experiment conditions and responses of pressure-leaching tests.

Standard Order	Experiment Order	Independent Variables			Responses
		Temperature ( $^{\circ}$ C; $x_{21}$ )	Pressure (bar; $x_{22}$ )	Residence Time (h; $x_{23}$ )	W Extraction (%)
1	13	220	15	2	84.45
2	19	212	15	2	84.44
3	20	220	18	2	89.89
4	21	212	12	2	86.18
5	22	228	18	2	87.74
6	23	220	15	1	75.68
7	24	220	15	1.5	83.06

The model's equation for zinc extraction ( $y_1$ ) adjusted to experimental data are present below in Equation (2):

$$y_1 = -43.2 - 0.51x_{12} + 206.7x_{13} + 0.12x_{12}^2 - 178.8x_{13}^2, \quad (2)$$

considering temperature ( $x_{12}$ ) and sulfuric acid concentration ( $x_{13}$ ) as independent variables.

For arsenic recovery, the model fitting did not achieve a statistically representative regression model with available data, so it was not possible to present it in this work. For tungsten extraction ( $y_2$ ), the adjusted model was a second-order regression model as in Equation (3) below:

$$y_2 = 112.7 - 9.74x_{22} + 44.7x_{23} + 0.339x_{22}^2 - 11.98x_{23}^2, \quad (3)$$

where pressure ( $x_{22}$ ) and residence time ( $x_{23}$ ) were the independent variables of  $y_2$ .

Analysis of variance (ANOVA) was performed in MINITAB, and the results are presented in Table 7.



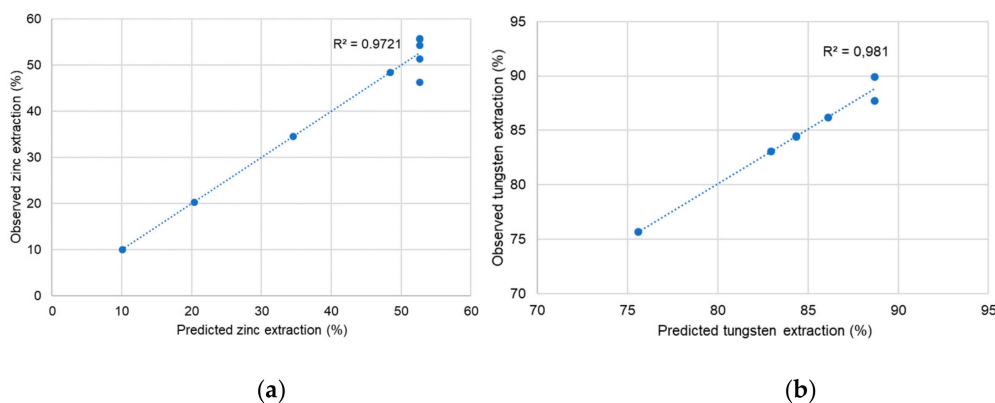
**Table 7.** ANOVA results of fitted models for zinc and tungsten extraction.

Metal Process	Source	Degree of Freedom	Sum of Squares	Mean Square	F-Value	P-Value
Zinc extraction	Model	4	2157.76	539.44	34.79	0.002
	Residual	4	62.03	15.51		
	Lack of fit	2	17.48	8.74	0.39	0.718
	Pure error	2	44.55	22.28		
Tungsten extraction	Model	4	119.974	29.994	25.80	0.038
	Residual	2	2.325	1.162		
	Totals	6	122.299			

Analyzing the ANOVA table, for the stirred-tank reactor tests, F-value  $F_0 = 37.79$  was higher than the F distribution of Snedecor with 0.05% significance. Thus, the model had significance; p-value = 0.002 was decidedly smaller than  $\alpha = 0.05$ , which confirmed a strong relationship between variables of temperature and sulfuric acid concentration with the response of zinc extraction. The lack-of-fit test showed a p-value 0.718 higher than the significance level, which confirmed that it did not count as evidence to reject the second-order regression model.

For the pressure-leaching model, a second-order regression model was also adjusted to tungsten extraction. The F-value of this model,  $F_0 = 25.80$ , was higher than the F distribution of the Snedecor with 0.05% significance; it can be inferred that the model had significance. The p-value = 0.007 was smaller than  $\alpha = 0.05$ , which confirmed a strong correlation between the variables of residence time with the response to tungsten extraction. The lack-of-fit test showed a p-value = 0.139 greater than the significance level, which confirmed that the second-order regression model was appropriate to represent the data.

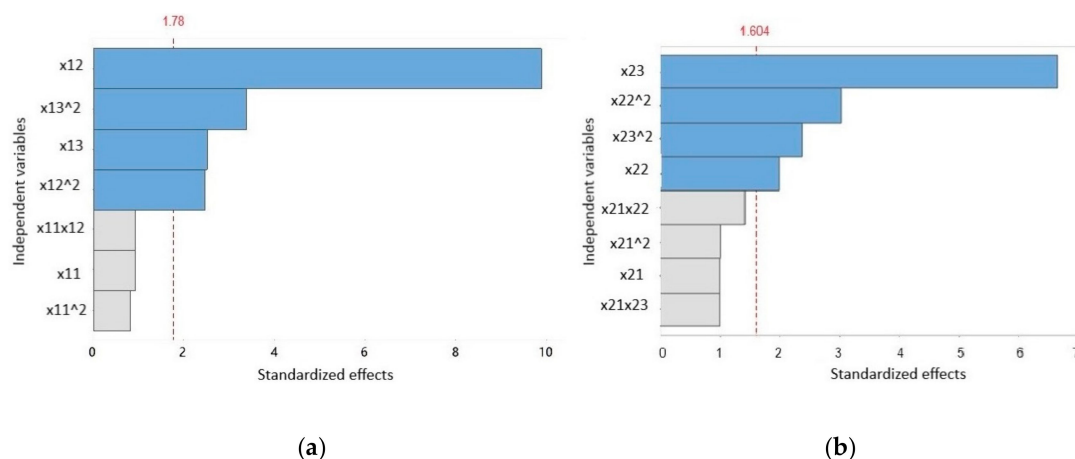
The actual data, or the observed data from the experiment tests, which were used to compare with the predicted model values for both zinc and tungsten extraction models are shown, respectively, in Figure 4a,b.



**Figure 4.** (a) Observed versus predicted responses of zinc extraction; (b) observed versus predicted responses of tungsten extraction.

Considering Figure 4a,b, the relation between the observed data and the predicted response on both models was above 95%. Usually,  $R^2$  is used to verify the goodness of a predicted model in experimental design [18]; however, as the data presented in this work were not set in a complete factorial design, some caution should be taken in the assessment of this parameter. In other words,  $R^2$  values might indicate variability in the predicted model responses. Alternatively, the predicted responses of zinc and tungsten extraction were not significantly different as the observed values.

t-Student distribution examined the statistical analysis of the variable models. Then, standardized effects were plotted as shown in Figure 5a,b for the zinc and the tungsten extraction models, respectively.



**Figure 5.** (a) Pareto chart of standardized effect of regression-model factors for zinc extraction. Note:  $x_{11}$ , solid ratio;  $x_{12}$ , temperature;  $x_{13}$ , sulfuric acid concentration. (b) Pareto chart of standardized effect of regression-model factors for tungsten extraction. Legend:  $x_{12}$ , temperature;  $x_{22}$ , pressure;  $x_{23}$ , residence time.

The Pareto charts with the absolute values of the standardized effects show all the effects on the response; these standardized effects are t-statistics. However, only standardized effects with values greater than the dashed line were statistically significant. In Figure 5a, the dashed line marks the 1.78 abscissa, for a 0.15% significance level (0.925 quantiles of t-Student distribution with four degrees of freedom). The statically significant variables and interaction factors, in this case, were  $x_{12}$ ,  $x_{12}^2$ ,  $x_{13}^2$ , and  $x_{13}$ . The greatest variable was temperature ( $x_{12}$ ) with t-value = 9.88, followed by the quadratic effect of sulfuric acid concentration ( $x_{13}^2$ ) with t-value = -3.39. The factor of sulfuric acid concentration ( $x_{13}$ ) and the quadratic effect of temperature ( $x_{12}^2$ ) had close t-values of  $\cong 2.5$ . According to the t-test, factors  $x_{11}$  and  $x_{11}^2$ , and interaction factor  $x_{11}x_{12}$  were not statically significant.

In Figure 5b, the dashed line marks the 1.604 abscissa for a 0.25% significance level (0.875 quantiles of t-Student distribution with four degrees of freedom). The variables and interaction factors that were statically significant in this case were  $x_{22}$ ,  $x_{22}^2$ ,  $x_{23}^2$ , and  $x_{23}$ . The most important variable was residence time ( $x_{23}$ ) with t-value = 6.64, followed by the quadratic effect of pressure ( $x_{22}^2$ ) with t-value = 3.03, factor pressure ( $x_{22}$ ), and the quadratic effect of residence time ( $x_{23}^2$ ). Considering the t-test, effects  $x_{21}$  and  $x_{21}^2$ , and interaction factors  $x_{21}x_{22}$  and  $x_{21}x_{23}$  were not statically significant, and could also be deleted from the model.

### 3.4. Response Surface

The contour plots for the zinc and tungsten extraction regression models are shown, respectively, in Figures 6 and 7.

Figure 6 shows that zinc extraction increased when the temperature of the stirred-tank reactor was between 70 and 80 °C. However, zinc extraction could be greater than 50% when the sulfuric acid concentration of the solution was around 0.45–0.75 mol.L<sup>-1</sup>. The solid ratio in the solution was not influenced by the zinc-extraction results at the operation conditions considered in this model.

Figure 7 presents the best tungsten-extraction results that could be achieved with pressure leaching at 17.5 bar. These results could be effective if the residence time of the solution was around 1.6–2.0 h. The pressure-leaching temperature had no significant effect on tungsten extraction at the conditions considered in this work.

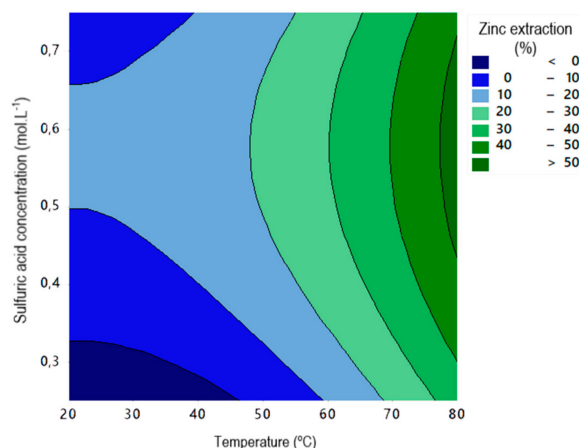


Figure 6. Variable temperature and sulfuric acid concentration of zinc-extraction response.

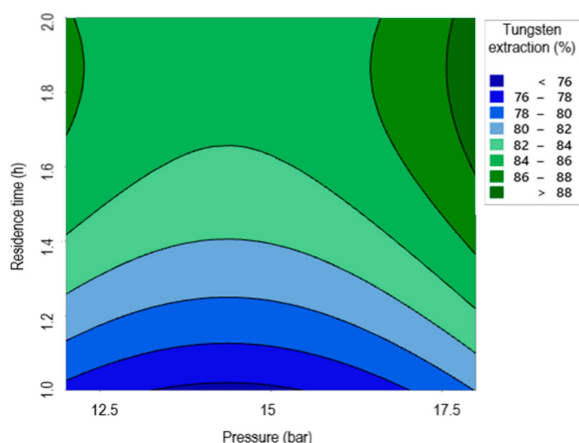


Figure 7. Variable pressure and residence time of tungsten-extraction response.

### 3.5. Conceptual Economic Results

The methodology for cost estimation of a re-mining project is similar but not identical to the one used for a new mine project. In capital and operating cost estimation, some parameters were not considered, and some were added, for example, existing infrastructure (roads, land, building, housing) that is available to be used. Furthermore, mining-development cost was considered as a minimum because the tailings are already exposed.

Academic software MAFMINE [25] was employed for the assessment of capital and operating costs. In Table 8, a summary of the capital cost estimation is presented.

Table 8. Summary of capital cost estimation for the re-mining project of Cabeço do Pião tailings.

Stage	Capital Cost (€) [min–max]
Re-mining	3,777,700–7,015,729
Reprocessing plant	5,950,248–11,050,460
Infrastructure	1,263,067–2,345,697
Total	10,991,015–20,411,886

The environmental costs of neo-tailings treatment and the tailings-storage facility, as well as the cost of restoration of the damaged area of Cabeço do Pião were not considered here because it lies outside the scope of this study. Operating cost estimation considers the average wage of mining-industry workers in Portugal; estimation results are shown in Table 9.

**Table 9.** Summary of operating cost estimation of the re-mining project of Cabeço do Pião tailings.

Stage	Operating Cost
Re-mining	3.49 (€/t tailings)
Reprocessing plant	7.14 (€/t ore product)
Electric power	10.66 (€/t ore product)
Electromechanical Maintenance	1981 (€/day)
General Service	5202 (€/day)
Administrative Services	1310 (€/day)

#### 4. Discussion

On the basis of previous results of the REMinE project [14,15], the physical–chemical characterization of tailings, and inferences from the social survey, we can conclude that tailings from Cabeço do Pião are a permanent environmental liability to the region and its residents.

A re-mining project through reprocessing techniques is feasible, and studies have worked with hydrometallurgical methods to recover metals from residues could ensure: studies of recovering copper from refractory flotation tailings reached over 86% efficiency [17]; reprocessing of cassiterite tailings by froth flotation with the addition of alternative reagents [26], proving that conventional flotation has better results. Around 70% of the cassiterite was recovered on the froth.

The performed experiment work and analysis of variance results showed that the selected models had significance and were well-adjusted to the available data; the variables had an influence on the model responses. However, a complete factorial design is recommended to ensure model stability, to calculate residuals (for lack of fit and pure error), and execute the pure quadratic curvature test [18].

The model response of zinc extraction ( $y_1$ ) was mostly influenced by temperature and  $H_2SO_4$  concentration in the stirred-tank reactor. The predicted optimal value of this response was 53.75%, near the maximum observed value of 55.77% that, with some experiment modification and precision, the residue could be reduced. At this optimum, the variable temperature of 80 °C and 0.55 mol·L<sup>-1</sup> of the medium acid was consistent with the literature [27]. Zinc extraction could be improved with the addition of a second stirred-tank reactor in series or by executing the operation in a pressure-leaching reactor.

Related to the flotation tests to recover the arsenic, these were performed in order to increase the complexity of the system and to be representative of the proposed reprocessing project [15]. However, as mentioned before, the regression model was rejected because no factor had statistical significance, and to maintain lower system variability.

The second model response obtained in this work was tungsten extraction ( $y_2$ ), which had influence on pressure leaching and residence time. The optimal spot predicted for this response was 83.09%, with 18 bar of pressure and 1.9 h of residence time. Tailings reprocessing to recover tungsten still lacks knowledge, but this project could be feasible considering the achieved extraction in the tests.

In a volume of 731,034 m<sup>3</sup> of available fine tailings to feed the reprocessing circuit, with a bulk density of 2230 kg·m<sup>-3</sup> [23], mean zinc content was 9.7 g·kg<sup>-1</sup> and mean tungsten content was 1.7 g·kg<sup>-1</sup>. The total mass of this metal in Cabeço do Pião was about 15,813 t zinc and 2771 t tungsten. Through the predicted extractions in the stirred-tank reactor and pressure-leaching tests, the total recovered mass could reach up to 8499 t of zinc and 2302 t of tungsten. Taking into account this total recoverable mass, preliminary economic conceptual analysis, and the price of zinc and tungsten at the current year, it could be that capital gain pays for the capital and operating costs, as well as other required investments.

#### 5. Conclusions

As proven in this work, a holistic approach is a highly complex complete overview of a system; in this case, sustainable development of the re-mining project involves environmental, social, and economic aspects. A holistic approach includes several stages in providing the appropriate information to support decision-makers [28] where many criteria are assessed. This methodology has the potential to be further used to evaluate other old tailings as directives and experimental references.

The goodness of the fitted regression models could ensure that the extraction responses are in a feasible region of the optimal conditions, and could be used to predict responses in other experimental conditions. Given the economic relevance on the commodities market—tungsten as a rare strategical metal and critical raw material [29], zinc as the third most consumed metal in the world—this project represents good investment.

At the same time, this kind of project has been performed to improve the life quality of residents in terms of environmental, social, and economic outcomes. Since the Cabeço do Pião dam is presently owned by a municipality, tailings re-mining is justified by higher metal prices and environmental reclamation [30] that allow the rejection of any capital-gain needs.

Therefore, the next stages to expand the holistic approach are to create a rehabilitation plan of environmental compartments and to elaborate the social-vulnerability risk as a social criterion.

**Author Contributions:** Conceptualization, J.F.; formal analysis, J.F. and M.C.V.; investigation, J.F., M.C.V., J.G., A.F. (Aurora Futuro), M.L.D. and D.M.; methodology, M.C.V., J.G., A.F. (Aurora Futuro), M.L.D., and D.M.; project administration, A.F. (António Fiúza); resources, A.F. (António Fiúza); supervision, M.C.V. and A.F. (António Fiúza); writing—original draft, J.F.; writing—review and editing, J.F., M.C.V., and A.F. (António Fiúza).

**Funding:** This research was funded by the Portuguese Foundation for Science and Technology, (FCT) (grants: ERA-MIN/0007 Improve Resource Efficiency and Minimize Environmental Footprint (REMinE), and UID/ECI/04028/2019 Centro de Recursos Naturais e Ambiente (CERENA)).

**Acknowledgments:** The first author is grateful for the financial support from the National Council for Scientific and Technological Development (CNPq)/Brazil (grant: 201144/2015-8).

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

## References

1. Tang, C.; Li, K.; Ni, W.; Fan, D. Recovering iron from iron ore tailings and preparing concrete composite admixtures. *Minerals* **2019**, *4*, 232. [CrossRef]
2. Castro-Gomes, J.P.; Silva, A.P.; Cano, R.P.; Suarez, J.D.; Albuquerque, A. Potential for reuse of tungsten mining waste-rock in technical-artistic value added products. *J. Clean. Prod.* **2012**, *25*, 34–41. [CrossRef]
3. Alcalde, J.; Kelm, U.; Vergara, D. Historical assessment of metal recovery potential from old mine tailings: A study case for porphyry copper tailings. Chile. *Miner. Eng.* **2018**, *127*, 334–338. [CrossRef]
4. Ilankoon, I.; Tang, Y.; Ghorbani, Y.; Northey, S.; Yellishetty, M.; Deng, X.; McBride, D. The current state and future directions of percolation leaching in the Chinese mining industry: Challenges and opportunities. *Miner. Eng.* **2018**, *125*, 206–222. [CrossRef]
5. Parbhakar-Fox, A.; Glen, J.; Raimondo, B. A Geometallurgical Approach to Tailings Management: An Example from the Savage River Fe-Ore Mine, Western Tasmania. *Minerals* **2018**, *8*, 454. [CrossRef]
6. Salifu, M.; Aiglsperger, T.; Hällström, L.; Martinsson, O.; Billström, K.; Ingri, J.; Dold, B.; Alakangas, L. Strontium (<sup>87</sup>Sr/<sup>86</sup>Sr) isotopes: A tracer for geochemical processes in mineralogically-complex mine wastes. *Appl. Geochem.* **2018**, *99*, 42–54. [CrossRef]
7. Filcenco-Olteanu, A.; Alakangas, L.; Fiúza, A.; Zlagnan, M.; Tomus, N. Physical chemical characterization of historical mining waste and ARD prediction tests. In Proceedings of the Mineral Engineering Conference MEC2017, E3S Web of Conferences, Wisła, Poland, 20–23 September 2017. [CrossRef]
8. Google Earth Pro V 7.3.2.5776. (June 6, 2017) Cabeço do Pião, Portugal. 40° 07' 40.74"N, 7° 38' 11.37"W, Eye alt 12.46 km. Digital Global 2019. Available online: <http://www.earth.google.com> (accessed on 30 August 2019).
9. Wheeler, A. Technical Report on The Mineral Resources and Reserves of The Panasqueira Mine, Portugal. 2016. Available online: [http://www.almonty.com/\\_resources/Panasqueira\\_43-101\\_Tech\\_Rep\\_Dec16\\_SEDAR.PDF](http://www.almonty.com/_resources/Panasqueira_43-101_Tech_Rep_Dec16_SEDAR.PDF) (accessed on 10 July 2019).
10. Ávila, P.F.; Silva, E.F.D.; Salgueiro, A.R.; Farinha, J.A. Geochemistry and mineralogy of mill tailings impoundments from the panasqueira mine (Portugal): Implications for the surrounding environment. *Mine Water Environ.* **2008**, *27*, 210–224.

11. Candeias, C.; da Silva, E.; Ávila, P.; Teixeira, J. Identifying sources and assessing potential risk of exposure to heavy metals and hazardous materials in mining areas: The case study of panasqueira mine (Central Portugal) as an example. *Geosciences* **2014**, *4*, 240–268. [CrossRef]
12. DGT, Direção Geral do Território. Carta Administrativa Oficial de Portugal. 2016. Available online: <http://dgterrirotiro.pt> (accessed on 22 January 2017).
13. Censos, Instituto Nacional de Estatística. 2011. Available online: [http://censos.ine.pt/xportal/xmain?xpgid=censos2011\\_apresentacao&xpid=CENSOS](http://censos.ine.pt/xportal/xmain?xpgid=censos2011_apresentacao&xpid=CENSOS) (accessed on 2 February 2018).
14. Figueiredo, J.; Vila, M.C.; Góis, J.; Biju, B.; Futuro, A.; Martins, D.; Dinis, M.L.; Fiúza, A. Bi-level depth assessment of an abandoned tailings dam aiming its reprocessing for recovery of valuable metals. *Miner. Eng.* **2016**, *133*, 1–9. [CrossRef]
15. Figueiredo, J.; Vila, M.C.; Matos, K.; Martins, D.; Futuro, A.; Dinis, M.L.; Góis, J.; Fiúza, A. Tailings reprocessing from Cabeço do Pião dam in Central Portugal: A kinetic approach of experimental data. *J. Sustain. Min.* **2018**, *17*, 139–144. [CrossRef]
16. Matos, K.N. Estudo da Lixiviação do Zinco como método de recuperação do material da barragem do Cabeço do Pião [Study of Zinc Leaching as a method of recovering material from the Cabeço do Pião dam]. Master's Thesis, University of Porto-Faculty of Engineering, Porto, Portugal, July 2017.
17. Bai, X.; Wen, S.; Liu, J.; Lin, Y. Response Surface Methodology for Optimization of Copper Leaching from Refractory Flotation Tailings. *Minerals* **2018**, *8*, 165. [CrossRef]
18. Montgomery, D.C. *Design and Analysis of Experiments*, 9th ed.; John Wiley Sons, Inc.: Hoboken, NJ, USA, 2017.
19. Vieceli, N.; Durão, F.O.; Guimarães, C.; Nogueira, C.A.; Pereira, M.F.C.; Margarido, F. Grade-recovery modelling and optimization of the froth flotation process of a lepidolite ore. *Int. J. Miner. Process.* **2016**, *157*, 184–494. [CrossRef]
20. Yang, J.; Shuai, Z.; Zhou, W.; Ma, S. Griding Optimization of Cassiterite-Polymetallic Sulfide Ore. *Minerals* **2019**, *9*, 134. [CrossRef]
21. Hustrulid, W.; Kuchta, M.; Martin, R. *Open Pit Mine Planning and Design. 1. Fundamentals*, 3rd ed.; Taylor & Francis Group: Leiden, The Netherlands, 2013; pp. 100–181.
22. Mancini, L.; Sala, S. Social impact assessment in the mining sector: Review and comparison of indicators frameworks. *Resour. Policy* **2018**, *57*, 98–111. [CrossRef]
23. Fiúza, A.; Vila, M.C. (Faculty of Engineering, University of Porto, Portugal). Análise quantitativa de risco ambiental e toxicológico relativa ao armazenamento de rejeitos de Cabeço do Pião [Quantitative analysis of environmental and toxicological risks related to the storage of tailings from Cabeço do Pião]. Personal communication, 2019.
24. Portuguese Legislation (Decret-Law n° 236/98 of 01-08-1998). Available online: <https://dre.pt/pesquisa/-/search/430457/details/maximized> (accessed on 30 August 2019).
25. Mafmine. Available online: <http://www.mafmine.com.br/v3/> (accessed on 3 September 2019).
26. Leistner, T.; Embrechts, M.; Leißner, T.; Chehreh Chelgani, S.; Osbahr, I.; Möckel, R.; Peuker, U.A.; Rudolph, M. A study of the reprocessing of fine and ultrafine cassiterite from gravity tailing residues by using various flotation techniques. *Miner. Eng.* **2016**, *96–97*, 94–98. [CrossRef]
27. Espiari, S.; Rashchi, F.; Sadrnezhad, S.K. Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy* **2006**, *82*, 54–62. [CrossRef]
28. Moldavska, A.; Welo, T. A Holistic approach to corporate sustainability assessment: Incorporating sustainable development goals into sustainable manufacturing performance evaluation. *J. Manuf. Syst.* **2019**, *50*, 53–68. [CrossRef]
29. Shen, L.; Li, X.; Lindberg, D.; Taskinen, P. Tungsten extractive metallurgy: A review of processes and their challenges for sustainability. *Miner. Eng.* **2019**, *142*, 105934. [CrossRef]
30. Edraki, M.; Baumgartl, T.; Manlapig, E.; Bradshaw, D.; Franks, D.M.; Moran, C.J. Designing mine tailings for better environmental, social and economic outcomes: A review of alternative approaches. *J. Clean. Prod.* **2014**, *84*, 411–420. [CrossRef]

