

1 Article

# 2 A Holistic Approach in Re-Mining Old Tailings 3 Deposits for The Supply of Critical Metals: A 4 Portuguese Case

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12 **Abstract:** The growth of demand for metallic minerals has faced with the need for new techniques  
13 and improving technologies for all mine life cycle operations. Nowadays, the exploitation of old  
14 tailings and mine wastes facilities could represent a solution to this demand, with economic and  
15 environmental advantages. W-Sn Panasqueira Mine has been operating for more than 100 years.  
16 Its first processing plant “Rio” was located near Zêrere river being the mineral processing residues  
17 deposited on the top hillside on the margin of this river in Cabeço do Pião tailings dam. The lack of  
18 maintenance and monitoring of this enormous structure in the last twenty years represents high  
19 risks to the environment and population of the surrounding region. The re-mining of the tailings by  
20 hydrometallurgical methods was considered, in order to satisfy these two enounced conditions -  
21 metals demand and environmental risk, aiming for the sale of the metal to pay the environmental  
22 intervention. Field samples campaign allowed collecting data and results from laboratory tests  
23 driving to use regression optimization. The re-mining solution was studied, taking into account the  
24 technical, economic, social, and environmental aspects.

25 **Keywords:** tungsten; zinc; tailings re-processing; multi-criteria optimization; modelling regression;  
26 Pareto optimal

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## 28 1. Introduction

29 Over years of mineral exploitation, millions of tons of mine waste and tailings were deposited,  
30 often incorrectly in the environment. The technology available decades ago and the lack of  
31 environmental control are factors that contributed to its indiscriminate disposal. However, tailings  
32 may be a source of minerals with high grades and supply metals with substantial economic value in  
33 the current mineral market. As the remaining metals contained in the solid phase of tailings not  
34 recovered at the time of its production represent potential resources, its re-processing could be an  
35 alternative to the global metal consumption in the perspective of sustainable mining [1].

36 Tailings dam is part of the legacy left by the intensive mining industry and frequently associated  
37 with environmental damage, social impacts, and possible failure of the dam. A holistic approach  
38 covers a complete overview with environmental, social, and economic aspects, could be efficient in  
39 the assessment of a re-mining project to all affected stakeholders. The European project ERA-MIN  
40 “REMinE: Improve Resource Efficiency and Minimize Environmental Footprint”, has been  
41 developed by institutions from three countries: Portugal, Romania, and Sweden that have a long  
42 history of mining activity in the last century. On its scope, the assessment of sustainable alternatives  
43 to tailings dam in these countries, as well the reprocessing of tailings, had been studied.

44 Cabeço do Pião dam, the Portuguese case study, has stored mining wastes and tailings from the  
45 ancient processing plant (“Rio”) which was belonging to the Panasqueira Mine Complex, presently

46 owned by the municipality of Fundão. The Panasqueira Mine, in exploitation for more than 100 years,  
 47 consists of a deposit of hydrothermal quartz-wolframite veins intruding into schists, known as Beira  
 48 schists, and shales [2]. It is also found cassiterite and chalcopyrite as ore minerals, associated with  
 49 arsenopyrite and pyrite.

50 The material stored in the dam, for more than fifty years, with harmful elements contents,  
 51 represents liabilities to environmental compartments and surrounding region and population.  
 52 Cabeço do Pião has a large volume roughly 1,900,000 m<sup>3</sup>, with an average height of 90 m and a steep  
 53 slope gradient up to 35° at the Zêrere's riverside. However, the material interesting to be recovered  
 54 is a fine tailing produced during the wolframite ancient processing, with a total 731,034 m<sup>3</sup> of the  
 55 volume discharged into the top of the dam.

56 The main aim of this work was to shown the progress of the re-mining of tailings, that is a highly  
 57 complex and ambitious project, involving different aspects: technical, economic, social, and  
 58 environmental. The reprocessing plant proposed by [3], which consists in two small modular circuits:  
 59 one to recover zinc through dynamic leaching; one to recover tungsten through pressure leaching,  
 60 this circuit involves, also, a primordial reverse flotation stage to eliminate sulfides on the froth. These  
 61 stages of the reprocessing plant were tested and evaluated technically through a methodology to  
 62 adjust the experimental data into multiple regression models. Then by the analysis of contour plots  
 63 locate the optimum results as an assessment of the project feasibility.

## 64 2. Materials and Methods

65 Many researcher methodologies were applied to study the abandoned mine site [4,5] aiming to  
 66 understand the properties and behavior of the tailings in the environment. A holistic approach  
 67 consists of an integrated assessment of all engaged parts of a project. To the re-mining project is  
 68 propose the assessment of environmental, social, technical and economic criteria on the scope of its  
 69 feasibility. The following methodology was applied to achieve these multiple criteria.

### 70 2.1 Field Research

#### 71 2.1.1 Social Survey

72 A social survey was developed and applied to obtain quantitative data of socioeconomic  
 73 characteristics of residents near the Cabeço do Pião dam. Surveys, interviews, or meetings with the  
 74 local community also aim to seek comprehension among stakeholders and obtain the social operation  
 75 license. The survey consisted of some objective questions, which included information about the  
 76 socioeconomic and health conditions of the interviewer's family. It comprised questions regarding  
 77 the perception of the risks and damages associated with the Cabeço do Pião dam, as well as  
 78 expectations regarding the solution of the problem.

79 Cabeço do Pião dam is in the countryside, in a scenario with several villages dispersed between  
 80 mountains. A small population which works in agriculture, mining and other activities are resulting  
 81 from it. The target population for this research was the residents of Cabeço do Pião village, of the  
 82 villages at upstream and downstream of the dam, also, of the Fundão Municipality (the current  
 83 responsible for the facilities of Cabeço do Pião). The villages, the total population, the total area, the  
 84 population density, and the distances of each village to Cabeço do dam are shown in Table 1.

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

Locality	Resident population	Area (Km <sup>2</sup> )	Population Density	Distances (Km)
Fundão (Municipalty)	29213	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
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86 <sup>1</sup>DGT-CAOP 2016, CENSOS 2011 [6, 7].

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88 This region has a part of the population which has no real existence, that is, hypothetical or  
89 difficult to find. Therefore, a non-probabilistic survey was considered, with the interviewees  
90 randomly selected. However, it was intended to interview a minimum of 10% of residents to reach a  
91 statistically significant survey.

## 92 2.1.2 Sampling

93 The tailings sampling campaign was conducted in the surface of Cabeço do Pião area, submitted  
94 to a regular rectangular mesh grid of approximately 40 by 20 m. The sampled area has about 2.6 ha,  
95 with a total of 33 demarcated points, their coordinates were determined by Global Position System  
96 (GPS) and georeferenced by Universal Transverse Mercator system (UTM). The sampling collection  
97 was performed at two different depths – 0.5 m and 2.5 m, totaling 66 samples.

98 These 66 tailings samples were submitted to chemical analysis (Energy Dispersive X-ray  
99 Fluorescence -XRF) and physical characterization (particle size distribution) according to the  
100 methodology described in [8]. In another stage of the project, two campaigns were carried out to  
101 collect leachates from the baseline of the dam, near the river, in March and June 2018. These  
102 leachates were physical and chemically characterized.

## 103 2.2 Experimental Research

### 104 2.2.1 Dynamic Leaching Tests

105 Dynamic leaching tests performed in a stirred reactor with a volume of 0.5 L, and average  
106 agitation speed of 225 rpm, on 0.1667 Kg of samples mass composed of a blend of two original  
107 samples from Cabeço do Pião tailings, selected according to the highest zinc content. The leaching  
108 tests were performed in acid medium, in a total of 0.25 L of a solution prepared using reagent: sulfuric  
109 acid (H<sub>2</sub>SO<sub>4</sub>) and ferric sulfate (Fe(SO<sub>4</sub>)<sub>3</sub>, 0.5 mol.L<sup>-1</sup>).

110 For each test, 0.02 L of the representative leach-liquor sample was taken from the reactor, after  
111 1, 2, 4 h, and at the end of tests at the 6<sup>th</sup> hour. All the leach liquor samples were filtered, the solid  
112 residues were analyzed in the XRF, and the liquors were analyzed by a flame atomic absorption  
113 spectroscopy [9].

114 The solid concentration, the temperature, and the sulfuric acid concentration were varied in each  
115 experiment; other leaching conditions were kept constant, in all the 9 tests performed. The objective  
116 of the dynamic leaching test was to extract zinc from tailings into a soluble liquor.

### 117 2.2.2 Flotation Tests

118 The flotation test was performed by a reverse route: roughing and scavenging, under fixed batch  
119 conditions, with pH adjusted to 4, and the chosen collector was MAXGOLD. The sample mass was  
120 approximately 1 Kg from Cabeço do Pião tailings blend, with a solid concentration of 0.3% (Kg.L<sup>-1</sup>).  
121 Air pressure was inserted at the roughing stage 8 L.min<sup>-1</sup>, and at the scavenging stage, the air pressure  
122 was 10 L.min<sup>-1</sup>.

123 The collector dosage and froth bed height were varied in each experiment; other flotation  
124 conditions were kept constant. The aim objective of the flotation was to recovery arsenic into the  
125 froth, as an intermediate stage of the reprocessing project, to reduce the sulfides in the material to be  
126 sent to the pressure leaching.

### 127 2.2.3 Pressure Leaching Tests

128 The pressure leaching was done in a high pressure-temperature reactor with 0.4 Kg of samples  
129 mass from Cabeço do Pião tailings. This stage has as chemical leaching reagent sodium hydroxide

130 (NaOH, 40 mol.L<sup>-1</sup>), the solid concentration was 0.5 % (Kg.L<sup>-1</sup>), and the speed rotation was 400 rpm.  
131 Also, the parameters pH and Eh were measured. After the leaching test, the liquor was filtered, and  
132 the solid residue was analyzed in XRF.

133 Among these tests, the temperature, pressure, and residence time of the experiment varied one by  
134 one. The objective of the pressure leaching was to extract tungsten from tailings into a soluble  
135 liquor.

### 136 2.3 Experimental Data Analysis and Modelling

137 It is known that factorial designs are efficiently used to study the response of experimental  
138 conditions in many experiments, as well described by [10]. When it is not possible to do an  
139 experimental design, the data obtained from experimental research could also be treated by  
140 regression methods. In many engineering problems, there are two or more variables (factors:  $x_1$ ,  $x_2$ ,  
141 ...,  $x_k$ ) related and affected the response (dependent variable:  $y$ ). The relationship between these  
142 variables could be fitting by a mathematical model named a multiple linear regression model [10],  
143 described by:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_k x_k + \epsilon, \quad (1)$$

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

146 In this study, to all experimental tests, the factors were chosen by results previously obtained in  
147 preliminary tests and kinetic studies [3] and were not put into codified values. In the first phase of  
148 fitting a regression model, the Analysis ToolPak add-in from Excel software was used, on a second  
149 phase, the Minitab software was required as an experimental data analysis tool.

150 The model fitting was performed using the least square method for estimating the regression  
151 coefficients. It was assumed that the error term  $\epsilon$  has  $E(\epsilon) = 0$  and  $V(\epsilon) = \sigma^2$ , which allows the  
152 hypothesis-testing procedures. As a requisition of the analysis, the statistical significance test of  
153 regression is useful to determine the linear relationship between the response variable  $y$  and the  
154 variables  $x_1$ ,  $x_2$ , ...,  $x_k$ . The confidence interval ( $1 - \alpha$ ) of this test was 95%, the analysis of the variance  
155 for the model was tested by the F-test and p-value, and the model inadequacy was assessed by a lack-  
156 of-fit F-test when it was possible. The hypothesis test was also used to adjust each regression  
157 coefficient ( $\beta_1$ ,  $\beta_2$ , ...,  $\beta_k$ ). Along, there were unplanned experiments the coefficient of determination  
158 ( $R^2$ ) could not measure the data variability.

159 The model adequacy, also important, was checked by the residual plot analysis, aiming to ensure  
160 that the fitted model is an adequate approximation to the true systems, and to verify that none of  
161 least squares regression is violated [11].

162 The response surface methodology (RSM) is used when several variables influence the response,  
163 and it is necessary to optimize this response. In other words, RSM is used to determine the best  
164 operation conditions in a series of experiments to obtain an optimal response. Through the prediction  
165 and verification of optimization conditions, a three-dimensional surface map is intuitively used.  
166 However, the contour plot, which is the projection of the response surface map, could be used to  
167 better visualization [11-13].

## 168 3. Results

### 169 3.1 Social Survey Inference

170 As expected, the inaccessibility of the population interfered in the quantitative results  
171 reasonably achieved. Many residents were not found on their houses, and some have reasons for  
172 refuse in to answer to the survey, such as lack of knowledge about the problem, or have an association  
173 with the mining company. Given this scenario, the few results obtained were treated qualitatively to  
174 obtain an overview of the problem, considering them as interviews.

175 The analysis of the interviews and conversations with the locals made it possible to understand  
 176 the reality of those who live nearby. It can be concluded that the population from the visited villages  
 177 are familiarized with a degraded landscape, that Cabeço do Pião does not being risks of rupture, and  
 178 water, soils, and dust contamination.

### 179 3.2. Physical-chemical characterization

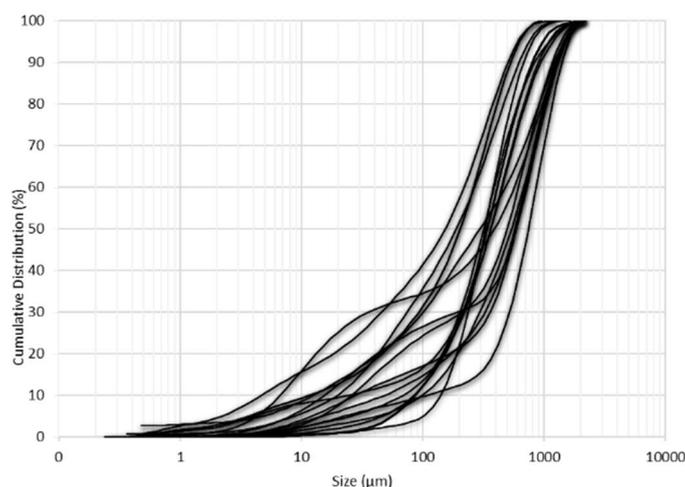
180 The XRF analysis results of the content of the detected metals are shown in Table 2 [8] as well  
 181 the descriptive statistics performed on the EXCEL® software package.

182 **Table 2.** Descriptive statistic of the chemical elements in tailings from Cabeço do Pião samples [8].

	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

183 The mean contents in % of weight, of the metals of interest to this work, are zinc 0.97 %, arsenic  
 184 13.55 %, and tungsten 0.17 %.

185 The particle size distributions of tailings samples from Cabeço do Pião dam is reported in Figure  
 186 1.



**Figure 1.** The particle size distribution of tailings samples from Cabeço do Pião dam.

187

188

189 The analysis of Figure 1 can be concluded that tailings material has a particle size less than 1000  
190  $\mu\text{m}$ .

191 The chemical analysis results of leachate from the tailings shown some divergences between the  
192 arsenic concentration on both sampling period, as shown in Table 3 [14].

193

**Table 3.** Leachates concentrations of tailings from Cabeço do Pião dam [14].

	Concentration ( $\text{mg.L}^{-1}$ )					
	Al	As	Cd	Cu	Mn	Zn
March	1150	99	0.44	44	138	59
June	113	6.3	0.45	37	252	55

194 This divergence could be explained by the different location of sampling on both periods, by the  
195 different climatic conditions of two seasons, and high seasonal variability typical of the sulfured  
196 tailings dam.

### 197 3.1. Regression modelling

198 Tables 4-6 present the experimental conditions and responses of zinc extraction, arsenic  
199 recovery, and tungsten extraction obtained in dynamic leaching, flotation, and pressure leaching  
200 tests, respectively.

201

**Table 4.** Experimental conditions and responses of the dynamic leaching tests.

Standard order	Run order	Independent variables			Responses
		S/L ratio ( $\text{Kg.L}^{-1}$ ) ( $x_1$ )	Temperature ( $^{\circ}\text{C}$ ) ( $x_2$ )	$\text{H}_2\text{SO}_4$ ( $\text{mol.L}^{-1}$ ) ( $x_3$ )	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

202

**Table 5.** Experimental conditions and responses of the flotation tests.

Run order	Independent variables		Responses As Recovery (%)
	Froth bed height (m)	Colector dosage (g.t <sup>-1</sup> )	
1	3	45	61.88
2	6	45	45.37
3	3	67.5	45.20
4	6	67.5	58.27

203

**Table 6.** Experimental conditions and responses of the pressure leaching tests.

Standard order	Run order	Independent variables			Responses W Extraction (%)
		Temperature (°C) (x <sub>1</sub> )	Pressure (bar) (x <sub>2</sub> )	Residence time (h) (x <sub>3</sub> )	
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

204

205

206

The regression model fitting was performed for estimating the regression coefficients, two-factor interaction, and quadratic terms were also included when it was possible. The model's equation for zinc extraction ( $y_1$ ) adjusted to experimental data are present bellow:

$$y_1 = -43.2 - 0.51X_2 + 206.7X_3 + 0.12X_2^2 - 178.8X_3^2, \quad (3)$$

207

considering the temperature ( $X_2$ ) and the sulfuric acid concentration ( $X_3$ ) as independent variables.

208

209

210

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

$$y_2 = 112.7 - 9.74X_2 + 44.7X_3 + 0.339X_2^2 - 11.98X_3^2, \quad (4)$$

211

where the pressure ( $X_2$ ) and the residence time ( $X_3$ ) are the independent variables of  $y_2$ .

212

213

The analysis of Variance (ANOVA) was performed in MINITAB, and the results are present in Table 7.

214

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

	Source	Degree of freedom	Sum of squares	Mean square	F-value	P-value
Zinc	Model	4	2157.76	539.44	34.79	0.002

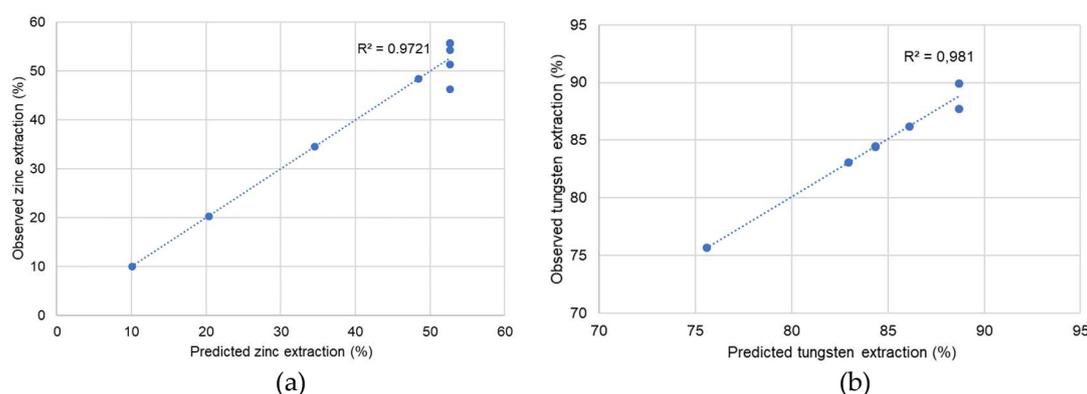
extraction	Residual	4	62.03	15.51		
	Lack-of-fit	2	17.48	8.74	0.39	0.718
	Pure error	2	44.55	22.28		
Tungsten	Model	4	119.974	29.994	25.80	0.038
extraction	Residual	2	2.325	1.162		
	Totals	6	122.299			

215 The F-values of tests are parameters for comparing the variance with the error variance and are  
 216 ratios of Mean Squares. Moreover, the p-values are the probabilities of the F-values statistics to be  
 217 exceeded [12]. The lack-of-fit (LOF) test was used to evaluate the adequacy of the models when it was  
 218 possible. It is worth mentioning that a variable is statistically significant when its p-value is small  
 219 than the significance level and could be identified in a Pareto chart with standardized effects.

220 Analyzing the ANOVA table, to the dynamic leaching, the F-value  $F_0 = 37.79$  is greater than the  
 221 F distribution of the Snedecor with 0.05 % of significance. Thus, the model has significance. The p-  
 222 value = 0.002 is very small than ( $\alpha=0.05$ ), which confirmed a strong relationship between the variables:  
 223 temperature and sulfuric acid concentration with the response of zinc extraction. The lack-of-fit test  
 224 showed a p-value=0.718 greater than the significance level, which confirms that it is no evidence to  
 225 reject the second-order regression model.

226 To the pressure leaching model, a second-order regression model was, also, adjusted to the  
 227 tungsten extraction. The F-value of this model,  $F_0 = 25.80$ , is greater than the F distribution of the  
 228 Snedecor with a 0.05 of significance, it can be inferred the model has significance. The p-value = 0.007  
 229 is small than ( $\alpha=0.05$ ) which confirmed a strong correlation between the variable, residence time, with  
 230 the response tungsten extraction. The lack-of-fit test showed a p-value=0.139 greater than the  
 231 significance level, which confirms that the second-order regression model is appropriated to  
 232 represent the data.

233 The actual data, or observed data from the experimental tests, was used to compare with the  
 234 predicted model values, to both model zinc extraction and tungsten extraction are shown,  
 235 respectively, in Figure 2a and Figure 2b.

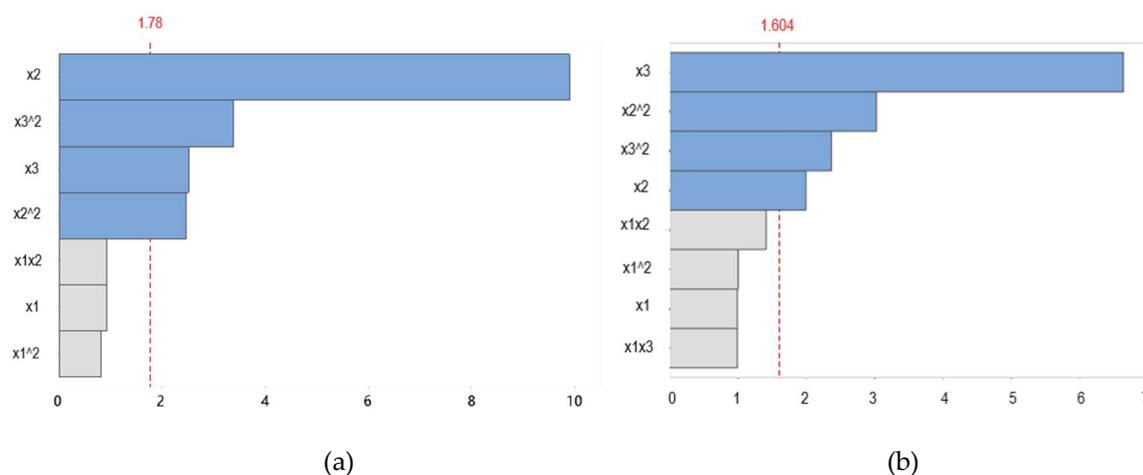


236

237 **Figure 2.** (a) Observed responses to zinc extraction versus predicted responses of zinc extraction; (b)  
 238 Observed responses to zinc extraction versus predicted responses of tungsten extraction.

239 Considering Figures 2a and 2b, the relation between the observed data and predicted response  
 240 on both models were above 95%. Usually the  $R^2$  is used to verify the goodness of the predicted model  
 241 in experimental design, however, as the data presented in this work was not set in a complete factorial  
 242 design, some precaution should be having in the assessment of this parameter. It is possible to see  
 243 that the predicted responses of zinc and tungsten extractions were not different as the observed  
 244 values.

245 The t-Student distribution studied the statistical analysis of the variable models, and then  
 246 standardized effects were plotted as shown in Figure 3a and Figure 3b, to the zinc and the tungsten  
 247 extraction models, respectively.



248

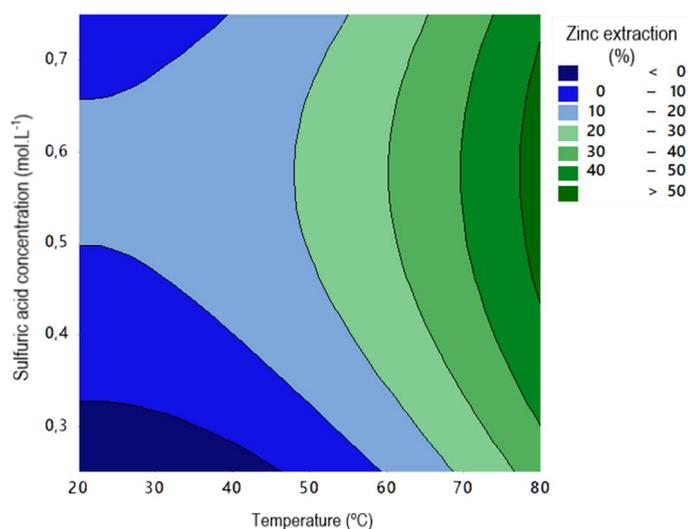
249 **Figure 3.** (a) Pareto chart of the standardized effect of the factors for the regression model for zinc  
 250 extraction. Legend  $x_1$ : S/L ratio;  $x_2$ : temperature;  $x_3$ : sulfuric acid concentration; (b) Pareto chart of the  
 251 standardized effect of the factors for the regression model for tungsten extraction. Legend  $x_1$ :  
 252 temperature;  $x_2$ : pressure;  $x_3$ : residence time.

253 The Pareto charts with the absolute values of the standardized effects show all the effects on the  
 254 response; these standardized effects are the t-statistics. However, only standardized effects with  
 255 values greater than the dashed line are statistically significant. In Figure 3a, the dashed line marks at  
 256 the abscissa 1.78, for the significance level of 0.15 % (the 0.925 quantiles of the t-Student distribution  
 257 with 4 degrees of freedom). The variables and interaction factors statically significant, in this case,  
 258 were the  $x_2$ ,  $x_2^2$ ,  $x_3^2$ ,  $x_3$ . Moreover, the greatest variable was the temperature ( $x_2$ ) with t-value = 9.88,  
 259 followed by the quadratic effect of the sulfuric acid concentration ( $x_3^2$ ) with t-value = - 3.39. The factor  
 260 sulfuric acid concentration ( $x_3$ ) and the quadratic effect of temperature ( $x_2^2$ ) had close t-values  $\approx$  2.5.  
 261 According to the t-test, the factors  $x_1$ ,  $x_1^2$  and the interaction factor  $x_1x_2$  were not statically significant.

262 In Figure 3b, the dashed line marks at the abscissa 1.604 for the significance level of 0.25 % (the  
 263 0.875 quantiles of the t-Student distribution with 4 degrees of freedom). The variables and interaction  
 264 factors statically significant, in this case, were the  $x_2$ ,  $x_2^2$ ,  $x_3^2$ ,  $x_3$ . Moreover, the most important variable  
 265 was the residence time ( $x_3$ ) with t-value = 6.64, followed by the quadratic effect of the pressure ( $x_2^2$ )  
 266 with t-value = 3.03, the factor pressure ( $x_2$ ) and the quadratic effect of residence time ( $x_3^2$ ). Considering  
 267 the t-test, the effects  $x_1$ ,  $x_1^2$ , the interaction factors  $x_1x_2$  and  $x_1x_3$  were not statically significant and  
 268 could be deleted from the model.

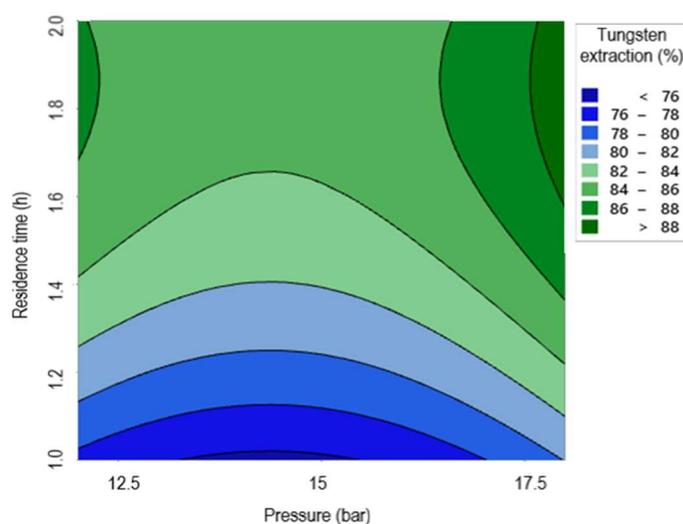
### 269 3.2. Response Surface

270 Through the response surface methodology (RSM) was possible to analyze the problems  
 271 presented in the previous session. The contour plots to the zinc extraction and tungsten extraction  
 272 regression models are shown, respectively, in Figure 4 and Figure 5.



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**Figure 4.** Contour plot of the variable temperature and sulfuric acid concentration of the zinc extraction response.



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**Figure 5.** Contour plot of the variables pressure and residence time of the tungsten extraction response.

279 Figure 4 shows that the zinc extraction increases when the temperature of the dynamic leaching  
280 is 70 °C until 80 °C. However, zinc extraction could be greater than 50 % when the sulfuric acid  
281 concentration of the solution is around 0.45 – 0.75 mol.L<sup>-1</sup>. The solid concentration in the solution was  
282 not influenced the zinc extraction results at the operations conditions considered in this model.

283 Figure 5 presents the best tungsten extraction results could be achieved with a pressure leaching  
284 at 17.5 bar. These results could be effective, if the residence time of the solution was around 1.6 – 2.0  
285 hours. The pressure leaching temperature has no significant effect on the tungsten extraction at the  
286 conditions considered in this work.

#### 287 4. Discussion

288 Based on previous studies [3,8], in the physical-chemical characterization results and inferences  
289 from the social survey, the tailings from Cabeço do Pião are a permanent environmental liability to  
290 the region and its residents.

291 The re-mining project through reprocessing techniques could be feasible, as well some  
292 researches have worked with hydrometallurgical methods to recover metals from residues: [10]  
293 studies of recover copper from refractory flotation tailings and has reached above 86% of efficiency;  
294 [15] has reprocessing cassiterite tailings by froth flotation and with addition of alternative reagents,

295 prove that the conventional flotation has better results, around 70 % of cassiterite was recovered on  
296 the froth.

297 The experimental analysis and analysis of variance results had shown that the selected models  
298 had significance and were well adjusted to the data available, the variables had influence on the  
299 model responses. However, a complete factorial design is recommended to ensure the model  
300 stability, to calculate the residuals (for the lack-of-fit and pure error), to execute the pure quadratic  
301 curvature test.

302 The model response of zinc extraction ( $y_1$ ) is greatest influenced by the dynamic leaching  
303 temperature and  $H_2SO_4$  concentration. The optimal value predicted of this response was 53.75 %, near  
304 to the maximum value observed 55.77 %, which with some experimental modification and precision  
305 the residual can be reduced. At this optimum, the variables temperature at 80 °C and 0.55 mol.L<sup>-1</sup> of  
306 the medium acid are consistent with the literature, as mentioned in [16]. The zinc extraction could be  
307 improved with the addition of a second dynamic reactor in series or execute the operation in a  
308 pressure leaching reactor.

309 Related to the flotation tests to recover arsenic, which were performed in order to increase the  
310 complexity of the system and in seek to be representative of the proposed reprocessing project [3].  
311 However, as mentioned before, the regression model was rejected because any factor has no statistical  
312 significance and to maintain the system variability lower.

313 The second model response obtained in this work was the tungsten extraction ( $y_2$ ), which has on  
314 influence of the pressure leaching and residence time. The optimal spot predicted of this response  
315 was 83.09 %, with 18 bar of pressure, and 114 minutes of residence time. The reprocessing of tailings  
316 to recover tungsten still lack knowledge, though, this project could be feasible considering the  
317 extraction achieved on the tests.

318 In view of the volume (731,034 m<sup>3</sup>) of fine tailings available to feed the reprocessing circuit and  
319 considering its bulk density to 2,230 kg. m<sup>-3</sup> [13], the mean zinc content as 9.7 g.Kg<sup>-1</sup> and the mean  
320 tungsten content as 1.7 g.Kg<sup>-1</sup>. The total mass of this metal on Cabeço do Pião are about 15,813 t of  
321 zinc and 2771 t of tungsten. To the extractions predicted on this work, the total mass recovered can  
322 reach up until 8,499 t of zinc 2302 t of tungsten.

## 323 5. Conclusions

324 As proven in this work, a holistic approach is a high-complex complete overview of a system; in  
325 this case, covers the environmental, social, and economic aspects. An integrated approach includes  
326 several stages, and the results shown in this work are a part of the whole.

327 The goodness of the fitted regression models could ensure that the extraction responses are in a  
328 feasible region and could be used to predict the responses in the whole system. As well as  
329 considerable metal content found in this material, and the economic relevance on the commodities  
330 market, this project might present a net economic gain. At the same time, could improve the life  
331 quality of the residents affected by constant environmental liabilities.

332 Therefore, the next stages of the approach are: 1) create a rehabilitation plan of the environmental  
333 compartments; 2) assess the operating and environmental costs of the project.

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337 Dinis; Supervision, M. Cristina Vila and António Fiúza; Writing – original draft, Janine Figueiredo; Writing –  
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