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Short Communication

Tailings reprocessing from Cabeço do Pião dam in Central Portugal: A kinetic approach of experimental data

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ABSTRACT

The mining waste and tailing dam are object of discussion due to the accidents that occur due to a lack of control or due to interest in the remaining minerals present in these materials. Most of the old tailings dams have high contents of heavy metals which could represent potential risks to the environment or be an alternative source of some critical raw materials. The case study of the Cabeço do Pião dam in Central Portugal involved tailings from a processing plant that belonged to the Panasqueira Mine Complex, which has been in operation for over 120 years. Waste rock and mining tailings were deposited in the area until 1995, and they represent an environmental liability for the local population due to their high content of toxic metals. Tailings reprocessing can be considered as a solution that minimizes social and environmental impacts, recovers some essential minerals, such as Zn, W, and Cu which can help to offset investments made. The project design involves several stages of metal concentration, determined by experiments, as well as a model of the process. The overall model will take into account technological constraints, social-economic conditions and environmental impacts. A preliminary result of an optimization study of the kinetic approach is presented in this piece of work.

1. Introduction

The low ore grades in recently found deposits and a shortage of essential metals have contributed to a higher volume of waste rock and tailings being produced during mining activity. Also, the global demand for metals and minerals has led to an increase in prices. However, the availability of mineral resources and their excessive consumption come together with an important fact, which is the inevitable depletion of non-renewable resources of raw materials (Dubiński, 2013). In this way, the traditional exploration model is becoming unsustainable, as the critical raw materials list has expanded over the years (EU, 2017). Further, sustainable management of mining activity involves safe waste disposal and reclamation of the total area affected.

Many mining sites, which are often abandoned, in Europe and worldwide have an old dam which has generated high impacts and presents several potential risks to the local community, contributing to a reduction in confidence in this industry. Deposited tailings originating from metallic mining, in particular, due to their sulfide content could result in the spread of this contaminant material through air or water to other regions. Sulfides when exposed to atmospheric conditions may be oxidized in a process known as Acid Mine Drainage (AMD), and this results in the successive formation of low pH effluents with several toxic metals (Kagambega, Sawadogo, Bamba, Zombre, & Galvez, 2014).

The leachates generated in AMD have a variable chemical composition because the geological background varies from site to site as well as over time for the same place. These heterogeneities of the tailing characteristics associated with geotechnical instabilities can generate a rupture followed by the failure of a dam.

New mining industry based on the use of alternative sources of energy and raw minerals, can consider the reprocessing of these tailings (EIT, 2017). Literature reports some pieces of work, such as (Liu & Huang, 2017; Lèbre, Corder, & Golev, 2017; Yin et al., 2018), obtained satisfactory results in metal recovery from mining tailings.

The objective of this paper is to present the progress of the tailing reprocessing model developed in the scope of the European project ERA-MIN "REMinE: Improve Resource Efficiency and Minimize Environmental Footprint". This project involves mines sites and institutions from three countries: Cabeço do Pião in Portugal, Sasca in Romania and Yxsjöberg in Sweden.

Although there is an extensive list of work concerning Cabeço do Pião (Ávila, da Silva, Salgueiro, & Farinha, 2008; Candeias, da Silva, Ávila, Coelho, & Teixeira, 2014; Candeias et al., 2013; Salgueiro, Ávila,

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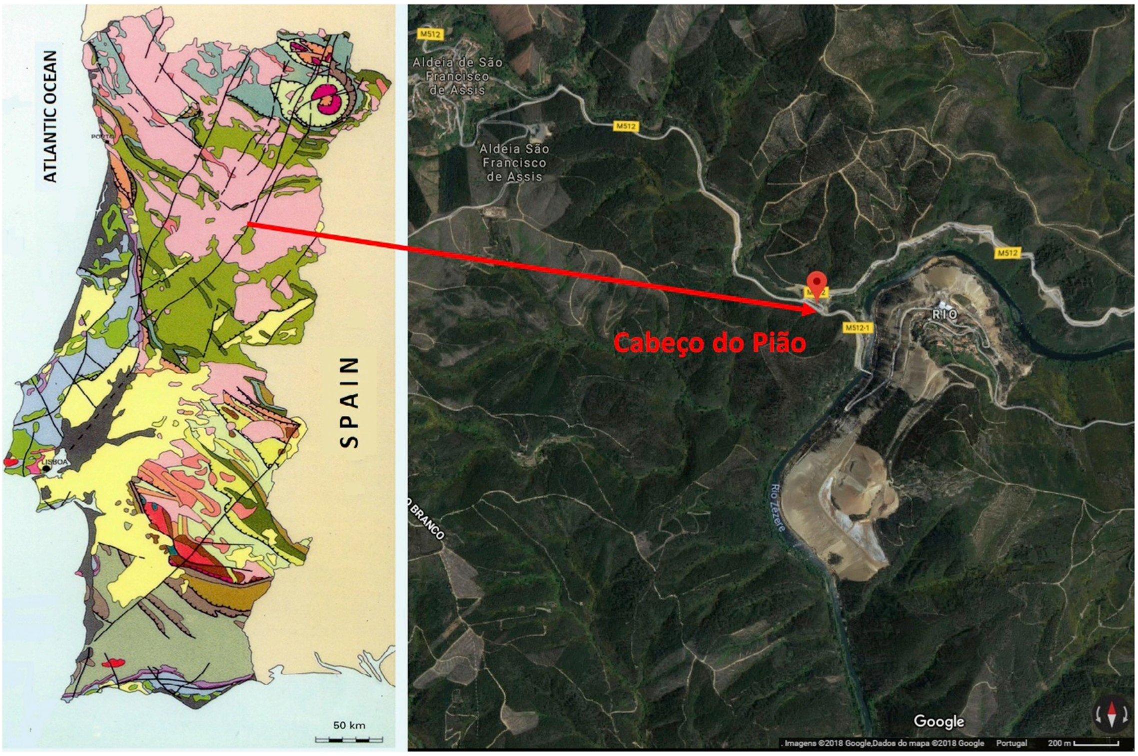

Fig. 1. a) Cabeço do Pião location in Portugal (IGM, 2010); b) View area (Google Earth, 2018).

Melo, & da Silva, 2013) which have primarily studied the geochemistry and mineralogy of these materials and the impacts in this area, however, none of these pieces of work ever considered tailing reprocessing as a permanent solution.

Reprocessing represents an option of recovering valuable metals present in the old dam. This work presents an approach regarding the elaboration of a model of optimization, to study the feasibility of this project. The research motivation is to seek a sustainable mining, with the generation of values to the society, the conservation and preservation of environmental compartments, as well as, sites remediation.

2. Case study

The area studies is Cabeço do Pião located in the Panasqueira Complex Mine area in Central Portugal (Fig. 1). The old dam was an open site for the deposit of waste rock and mining tailings. It was built on the riverbanks of the Zêrere and poses potential risks to the surrounding area and watercourses.

Over 70 years Cabeço do Pião received residues from the Panasqueira Mine, among them were coarse material and sludge. Mostly, the materials consist of schists and quartz, with a lower percentage of pyrite and arsenopyrite (Wheeler, 2016). The tailing dam shows a degraded landscape accelerated by the frequent adverse climatic conditions in this region. The predominantly fine grain size of these materials creates highly specific surfaces which are available for chemical reactions and AMD generation.

It is estimated that a total of more than 8 million tons of material was deposited in the tailing facilities of Panasqueira's mine, occupying an extensive area (Wheeler, 2016). These residues have high concentrations of metals, namely Cu, Zn, W and especially As.

3. Materials and methods

A field sample campaign was performed according to a regular grid of the topsoil of the Cabeço do Pião dam in an area of about 2.6 ha. In total, 66 samples were collected at two topographic levels: on the surface (up to 50 cm depth) and at depth (approximately 2–2.5 m). GPS (Global Position System) was used to determine the coordinates of the samples and the georeferenced was done using the UTM (Universal Transverse Mercator) system.

3.1. Chemical analysis

Firstly, tailings samples were submitted to the preparation stage, in conformity with the requirements of the experiment bellow.

The material was analyzed using the Energy Dispersive X-ray Fluorescence (XRF) method to determine the metal contents using the X-MET8000 Oxford instrument. The mean results of the chemical analysis were within 95% confidence limits of the recommended values given for the certified materials. The Relative Standard Deviation was between 0% and 5%. Interesting elements were detected, such as As, W, Zn, Cu, and Fe which are shown in Table 1.

4. Preliminary model formulation

The definition of the reprocessing technologies, applicable to this material, is based on the physical, chemical and mineralogical characteristics that constitute a guide to distinguishing between primary and secondary minerals. As these materials resulted from the ore processing plant, mainly through the tungsten recovery process, where the addition of several reagents takes place, including sulfuric acid, lime, cresylic acid, pine oil and fuel oil (Wheeler, 2016), a predominance of secondary minerals is expected. These tailings are exposed to open air and experience the impacts of weather and this contributes to the transformation of the material characteristics.

Laboratory characterization plays an essential role in defining the

Table 1
Chemical analysis of tailings from Cabeço do Pião dam (ppm).

	As	W	Zn	Cu	Fe
Mean	143041	2496	99944	4738	238389

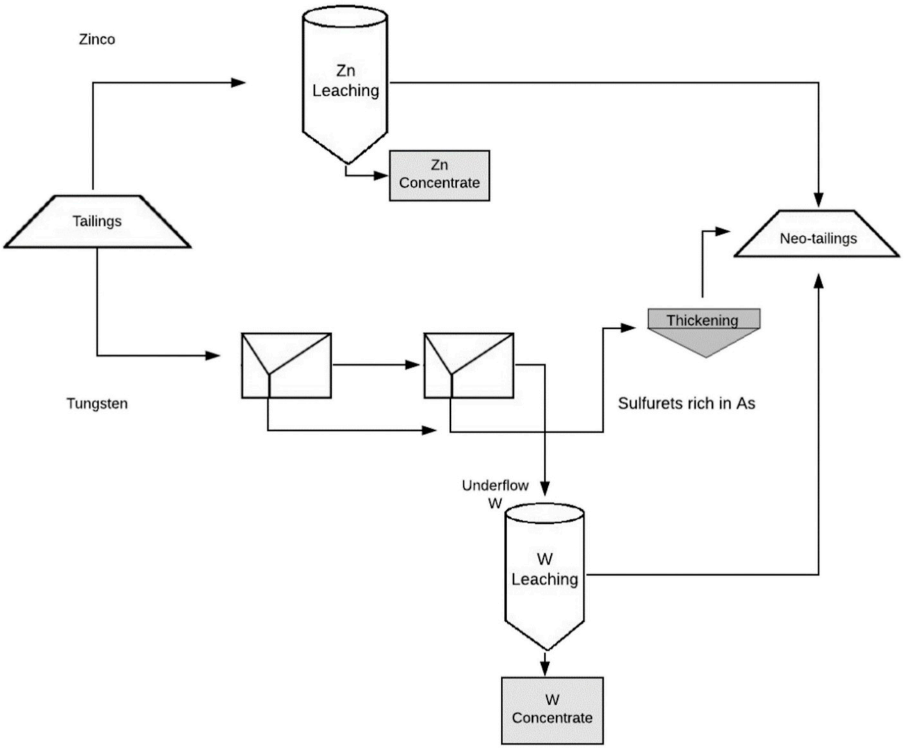

Fig. 2. Qualitative flowsheet of reprocessing tailings from Cabeço do Pião.

real situation of Cabeço do Pião. Considering the variable composition of the material, reprocessing them using physical and hydrometallurgical techniques appears to be a promising alternative.

The reprocessing flowsheet proposed (Fig. 2) considers the properties of the materials in addition to the initial results from the laboratory tests and the geostatistical study performance based on chemical analysis.

In a conceptual project it is essential to know the initial restrictions in order to delineate its structure. This involves the following:

1. The definition of the exploitation methods and transport of the material from the original site to the reprocessing plant.
2. The spatial distribution of metal concentrations which is used to define two different zones: one rich in zinc and another rich in tungsten, affording two reprocessing circuits – the Zn circuit and the W circuit.
3. For the Zn recovery circuit, dynamic leaching was suggested (Matos, 2017).
4. For the W recovery circuit, a two-stage reverse-flotation process is recommended. In the first flotation stage the goal is to obtain on the underflow an ore pulp with the lowest content of As, which is directed to the second flotation bank cells. The overflow rich in arsenic will be sent for the thickening process to compound the neo-tailings dam.
5. In the second flotation cell, the underflow with rich tungsten content is discharged into the leaching stage. The overflow is a neo-tailing rich in sulfides.
6. In continuing the tungsten circuit, the pulp obtained in the flotation will be leached in a dynamic reactor to achieve a maximum metal grade.
7. The tailings from the flotation circuit will be thickened and will compound the neo-tailings dam.

The entire project design consists of various stages, which involve several decision variables subject to constraints, represented by multi-objective functions that should be optimized to agree with optimal system performance. The sustainable and integrated project management consists in searching for an adequate solution close to the global optimum.

The reprocessing unit operation: leaching and flotation models are presented in an optimization low complexity level. Additionally, with the use of the experimental data, it was possible to develop and validate the kinetic models. The methodology to be used in the leaching and flotation process involved studying a mathematical model which describes the time performance of the process products, outlined in the diagram below (Fig. 3) (Vila, 1995):

5. Leaching tests and modeling

In this study, the experimental data was obtained through leaching tests, using samples from Cabeço do Pião, in work developed by (Matos, 2017). These were tests executed in a dynamic reactor whilst leaching in acid medium.

The tests were performed on samples composed of a blend of two original samples, which were selected due to them having the highest zinc content, i.e. **A9_P** and **B10_P**, with 22 900 ppm and 27 800 ppm, respectively. The chemical analysis of the sample blend, by XRF, is shown in Table 2 (Matos, 2017).

The leaching experiments were carried out on 0.1667 Kg of sample mass, in a reactor with a total volume of 0.5 L. The volume of the solution was 0.25 L and the solid concentration equalled 0.4% (Kg L^{-1}). The average agitation speed was 225 rpm, and the average temperature was 80 °C. Leaching solutions were prepared using reagent, sulfuric acid (H_2SO_4) and ferric sulfate ($Fe(SO_4)_3$) with concentrations of 0.5 M (Matos, 2017).

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 the 6th hour. All the leach liquor samples were filtered. The solid residues were analyzed in the XRF, and the liquors were analyzed by a flame atomic absorption spectroscopy (Matos, 2017). As expected the mass of dissolved Zn in the solution increased over time, and at the 6th hour it had a metal content of 10 000 ppm. The leached chemical analysis, at the

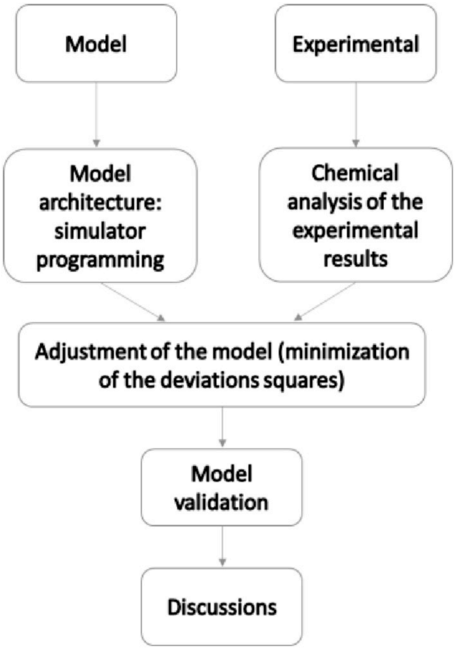

Fig. 3. Modeling methodology (Vila, 1995).

Table 2
The chemical analysis of the sample blend (ppm).

Sample	As	Fe	Zn	Cu
(A9_P + B10_P)	172 558	278 145	24 295	7602

Table 3
Leached chemical analysis (ppm) (Matos, 2017).

Leached	As	Fe	Zn	Cu
sample	8800	77 000	10 000	456

end of the test, is shown in Table 3.

The dissolution process of the ZnS could be controlled by two reactions (Eq. (1) and Eq. (2)) (Dutrizac & Macdonald, 1978):

$$ZnS_{(s)} + H_2SO_4 \rightarrow ZnSO_{4(aq)} + H_2S_{(l)} \quad (1)$$

$$Fe(SO_4)_3 + H_2S \rightarrow 2FeSO_4 + H_2SO_4 + S^{o}_{\ (s)} \quad (2)$$

During the oxidative leaching of ZnS, sulfur would be formed principaly in sulfate, around 85%–95% of the sulfide is oxidized into elemental sulfur. However, during the initial step of dissolution, the quantity of S produced is deficient, therefore the diffusion resistance is small in dynamic leaching which is considered a first-order kinetic model (Dutrizac & Macdonald, 1978). During the second step, the ferric sulfate contributes to the chemical reaction of the S and leads to the subsequent increase of Zn dissolution. Additionally, this is a heterogeneous process in the reactor and the concentration variation of any species relative to residence time is usually empirical, based on experience and knowledge about the reaction (Fiúza, 2003). The Zn content in the solid residues was calculated following the kinetic empirical leaching model, Equation (3):

$$(dMZ/dt) = WZ_o - WZ - KMZ \quad (3)$$

where W (kg s^{-1}) is the mass flow rate inside and outside of the reactor; Z (g kg^{-1}) is the zinc concentration in the solid residue; Z_0 (g kg^{-1}) is the feed concentration in the sample; M (kg) is the solid mass inside the reactor, and K_L (g kg^{-1} s^{-1}) is the kinetic leaching reaction constant.

Table 4
Chemical analysis from flotation feed sample (ppm).

Flotation	As	W	Zn	Cu
sample	168300	3708	14335	6191

The resolution of Equation (3) by a linear differential equation of first order, that gives the estimate of the metal content in the solid residue, as explicit in Equation (4):

$$Z = (\tau Z_0 \exp((K_L\text{-}\tau)t) + K_L Z_0 \exp(\text{-}\tau t))/(\exp(K_L t)\ (\tau + K_L)) \quad (4)$$

where τ (s^{-1}) is the time constant.

Thus it is possible to calculate the Zn dissolved mass in the liquor and also to determine the metal recovery.

The leaching kinetic constant K_L is then obtained through optimization by minimizing the squared deviations between the experimental and simulated values of the Zn content.

6. Flotation test and modeling

A substantial volume of the collected sample was reserved to be used in batch flotation tests. The chemical analysis of the feed to the flotation made by XRF is presented in Table 4 with the most critical heavy metals.

The flotation test was performed by a reverse process aiming to recover the maximum As in the froth as a gangue. The flotation circuit was composed of two stages: roughing and scavenging, under fixed batch conditions, with pH adjusted to 4. The sample mass was approximately 1 kg, with a solids content of 0.3% (kg L^{-1}) and a froth bed height of 0.06 m. In the roughing stage, the air pressure was 8 L min^{-1}, and the collector (MAXGOLD) dosage was 45 g t^{-1}. Finally, in the scavenging stage, the air pressure was 10 L min^{-1}, and the collector (MAXGOLD) dosage was 22.5 g t^{-1}.

The As removal from the pulp was a result of the selective transfer of sulfides from the pulp to the froth by a particle-bubble attachment (Mowla, Karimi, & Ostadnezhad, 2008). It is assumed that a mass disappearance in respect to the floatable particles in the pulp takes place. The rate of disappearance of particles mass (-dW/dt) should be proportional to the mass of those particles in the cell (W). The batch flotation model is often controlled as a first-order process, with the kinetic constant given by Equation (5) (Wills & Finch, 2016):

$$(\text{-}dW/dt) = K_f W \quad (5)$$

where K_f (s^{-1}) is the flotation kinetic constant; t (s) is the pulp residence time and W (Kg) particle mass in the cell. Even low flotability particles, such as tungsten, can collide and attach as a bubble and be dragged into the pulp. Thus, the initial mass of a mineral species (W_0) will be greater than the final mass of the particles in the batch.

The flotation kinetic constant will be optimized by minimizing the squared deviations between the experimental and the simulated model values of the metal mass present in the pulp. Moreover, the recovery of any mineral species in the froth is given by Equation (6) (Wills & Finch, 2016):

$$R = 1 - \exp(\text{-}K_f\ t) \quad (6)$$

7. Results and discussions

7.1. Leaching model

In the evaluation of the kinetics of leaching, the results obtained (experimental and model simulation) are given in Fig. 4, where the mass of zinc leached is plotted against time. Moreover, the Zn recovery from the rich liquor is plotted in Fig. 5.

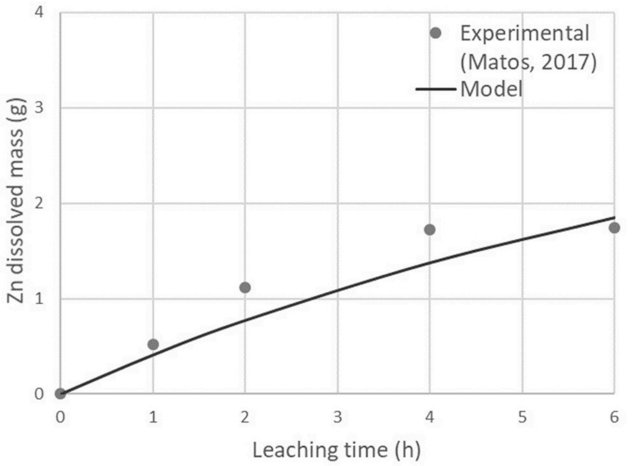

Fig. 4. Zn mass leached over time.

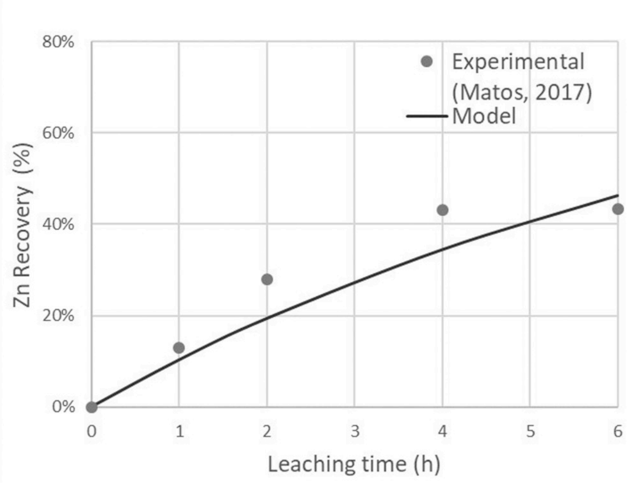

Fig. 5. Zn recovery over time.

The values found for zinc dissolved mass were very close to each other, with the average being 1.79 g in the liquor. The modeling results give $K_L = 0.091\ \mathrm{g\,kg^{-1}\,h^{-1}}$, which permits model recovery of around 46%. However, the experimental recovery was 43.4% (Matos, 2017). The small difference between these values can be explained by experimental errors.

7.2. Flotation model

In this study the tungsten flotation performance for the lowest values of K_f was evaluated To obtain recovery with the smallest possible tungsten mass within the froth. The results obtained (experimental tests and kinetic model) are represented in Fig. 6, (1-R) *vs.* flotation time (min).

The disappearance plot means that the tungsten mass that is carried to the froth decreases over time. The difference between the model and the experimental results is small; both had a recovery of around 70%. Besides, the modeling resulted in $K_f = 0.0327\ \mathrm{min^{-1}}$, regarding to the small fraction of floated tungsten.

The mark "Pulp" refers to experimental results obtained at the end of the flotation stage. At that time, the tungsten grade in the pre-concentrate was around 5490 ppm based on the initial metal content (3708 ppm) and the recovery was 64.54%. According was outlined in the qualitative flowsheet reprocessing (Fig. 2), this pre-concentrate will be leached to recover tungsten in future work.

It is fundamental to recognize As recovery since its elimination guarantees the purity of the pre-concentrate. Although, this process will produce tailings with a higher As content, which should be appropriately stored by technologies that maintain the safety of the neo-tailings deposit. The As recovery is plotted in Fig. 7.

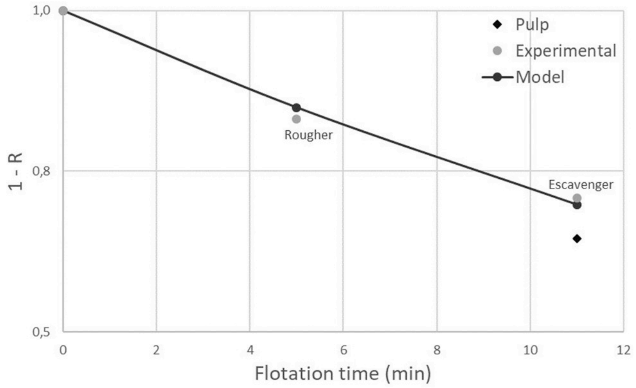

Fig. 6. Disappearance plot of tungsten in the pulp.

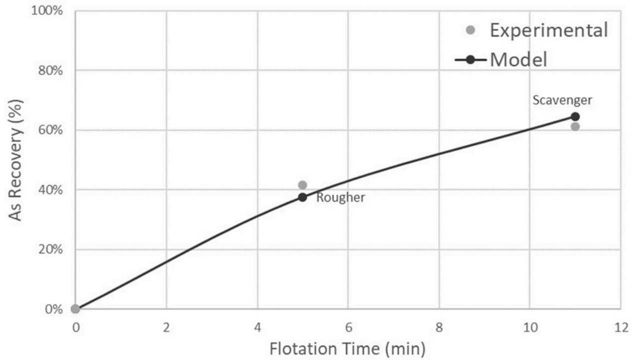

Fig. 7. As recovery over time.

The As modeling gives a recovery of around 64.54%, in comparison to experimental data which was 61.21%. It is noticeable that the model adjustment leads to higher metal recovery at the scavenging stage, although it is very close to the experimental data. Finally, the modeling results enable $K_f = 0.0942\ \mathrm{min^{-1}}$, considering the total As floated.

8. Conclusions

This paper is a preliminary proposal for the optimization of multi-objective criteria to evaluate the feasibility of the tailing reprocessing from Cabeço do Pião dam.

The outcome achieved, with the first model formulation, confirm that it is necessary to evaluate all the prevailing parameters at each stage of the reprocessing to find the optimal kinetic constant.

The general problem formulation, considering a mathematical, technological and economic approach, requires that all reprocessing be optimized, this is one of the elaborate challenges faced by the proposed management tool. Additionally, any techniques could be discussed to follow the best solution to this project.

Ethical statement

Authors state that the research was conducted according to ethical standards.

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Conflict of interest

Authors state that there is not any conflict of interest.

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