Metal recovery from flotation tailings

Zinc flotation – Panasqueira Mine

Summary of dissertation for the degree of Master in Geological and Mining Engineering

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Abstract

The concept of circular economy can be applied to mineral exploitation in ways such as the increasing of production of secondary mineral by-products, which creates more complete value chains and optimizes the use of the available resources, while generating less waste.

This work focused on zinc recovery from tailings with high arsenic content, using the froth flotation method for the separation of minerals. The studied sample contained 5.59% Zn, 18.74% As, and 0,20% Cu. In order to design the laboratory experimental plan, a factorial design using a Taguchi orthogonal array L8(2^7) was chosen, where four two-level factors were tested, with one replication of the design and four tests at the centre point, totalling at 20 tests. The controlled factors were pH, pulp aeration, dosage of collector, and dosage of activator.

The tests allowed for the increase in Zn and Cu grades across all trials, while reducing As grade, resulting in the average recoveries of 61,42% Zn, 25,52% As and 84,46% Cu. Even though the objective in conducting the trials was the flotation of zinc, the recovery of copper was superior, however its grade remained comparatively low, not surpassing 0.80%. The selectivity index between Zn and As was calculated, that measures the separation between two elements in froth flotation.

The factorial design using Taguchi's orthogonal arrays allowed to identify the statistically significant factors that influence the four chosen response values (Zn, As, and Cu recoveries, and the selectivity index between Zn and As). It was discovered pH and pulp aeration were the significant factors that influenced three of the analysed response factors (Zn recovery, Cu recovery and the selectivity index), showing a possible correlation between Zn and Cu, and that pH and the collector dosage were the significant factors regarding the recovery of As.

Using linear regression, a model explaining As recovery in the design space was achieved. The other responses were unable to be modelled due to curvature. The existence of curvature requires the expansion of the experimental plan, i.e. conducting more trials, in order to estimate the higher order terms.

The results show that the applied methodology was effective in identifying the significant factors that influence each metal's recovery. Besides the expansion of the experimental plan, other future works are suggested, such as testing other sets of reagents and the conducting of reverse flotation trials.

Keywords: Zinc, arsenic, flotation, recovery, selectivity, Taguchi

1. Introduction

The mining industry has been, since time unknown, the driving force behind the origin of most materials that benefit society in the ways of technological development. All the while, the industry promotes economic growth, employment, and the development both of local communities, and at a national level, through the collection of income tax.

In order for the EU to be economically competitive and reach the goals of mineral resource self-sufficiency, while preventing unnecessary environmental damage, a careful attention must be given to the concept of Circular Economy, where the maximization of efficiency regarding the use of the available resources takes a high priority. This concept should be applied to the mining industry in several ways, namely by increasing the production or by taking better advantage of the mineral by-products, which allows for the creation of more complete chains of value.

The theme of this paper relates to the aforementioned topics in that its objective was the separation of zinc from the arsenic-rich flotation tailings of the copper processing circuit of Panasqueira Mine, operated by Beralt Tin and Wolfram (Portugal) S.A.

The removal of arsenic from concentrates is crucial. It is considered a penalty element for in smelting due to the high cost of tailings control, that are highly pollutant due to waste discharges and causing H_sSO_4 emissions (Valdivieso et al. 2006).

Vreugde (1982) showed that recovery arsenopirite (FeAsS) is lower when a pH value upwards of 7.5 is used in the froth flotation pulp, being lower still at 10.5 pH. It was also shown by Vreugde (1982) and Asian et al. (2003) that the oxidation caused by pulp aeration plays a major part in the depression of arsenopyrite. Lin et al. (2018) demonstrated that $Ca(ClO)_2$ and SH, when added as depressants, can indeed reduce arsenopirite flotation, and Vreugde (1982) had success using H_2O_2 and NaClO to the same effect.

Regarding zinc flotation, it's common practise do use $CuSO_4$ as an activator (Michaud, 2015), as the copper ions in the sulphate form a film around the zinc particles which react favourably to collectors destined for sulphide flotation. Asian et al. (2003) noted that aeration of the pulp and the adition of CaO had a positive effect on zinc flotation. The pH reccomended for zinc flotation is between 10 and 12 (Michaud, 2015).

In order to conduct the experiment, a factorial design was implemented using Taguchi's orthogonal arrays. This method has advantages when applied to froth flotation due to the fact that flotation systems are often complex, and a high number of factors, both controllable and noise factors may affect the results. Even more so, interactions between factors might play a crucial role in froth flotation (Blanco, 2016) (Salerno et al., 2018), and this type of experimental design allows for the study of factor interactions, as well as allowing for the least amount of trials in order to properly study the factor's effects on the response values.

2. Methods

2.1. Ore Characterization

The sample used in this study consisted of tailings from the Panasqueira Mine copper processing circuit. Sample granulometry was 80% < 75 μm. The sample was analysed through x-ray spectroscopy, a non-destructive technique that allows for the identification and quantification of the elements present in a sample. The target elements were Zn, As and Cu, which were also the ones searched for in the flotation results. It was found the sample had 5.58% Zn 18.74% As.

2.2. Factor identification

Preliminary tests were first conducted in order to develop knowledge of the flotation process and to help in identifying the factors to add to the factorial design.

Several controllable and uncontrollable factors were identified, listed below:

- Controllable factors: Flotation cell volume; Percent solids by weight; Collector dosage; Reagent addition order; Conditioning time; Pulp pH; Cell rotation speed; Pulp aeration.

- Uncontrollable factors: Material oxidation; Ambient temperature; Pulp temperature; Airflow rate; Froth column height.

Of these, the factors included in the factorial design were:

- Pulp pH;
- Pulp Aeration;
- Collector dosage;
- Activator dosage.

These factors were selected based on the observations made during the preliminary tests, but also as they are commonly cited as being some of the more influential factors in froth flotation studies, in works such as Salerno et al. (2018), Figueira (2018), Blanco, (2016), Aksani & Mian (2001). Furthermore, regarding the objectives of the experiment, these factors were considered of importance due their importance in the flotation of zinc and depression of arsenic.

Operational conditions for the factors were selected based on information in the previous works and from *Mining Chemicals Handbook, Revised Edition* (Cytec Industries Inc., 2002), and are presented in Table 1.

Table 1. Factors selected and their levels

Factor	Low level	High level
pH	9	12
Aeration	0 min	30 min
Collector	1 g/t/%Zn	2 g/t/%Zn
Activator	200 g/t	500 g/t

The reagents used in the flotation process were

- Copper sulphate as activator ($CuSO_4$);

- Aerofloat 211 (ditiophosphate) as collector;

- Aerofroth 65 (polypropylene glycol) as frother;

- $Ca(OH)_2$ as pH regulator.

In order to evaluate flotation performance, the responses selected for the analysis were the Recovery of the elements analysed (Zn, As, Cu) which is given by equation 1

$$R_{i,f}(\%) = \frac{m_{i,f}}{m_{i,a}} * 100 \qquad \text{(Equation 1)}$$

where $R_{i,f}$ denotes the recovery in floated product of element *i*, $m_{i,f}$ the quantity (mass) of said element in the floated product *f*, and $m_{i,a}$ the element's feed mass.

The recovery gives a measure of the element's floatability in the froth flotation process and it can be compared between the several elements in the floated product in order to understand the efficiency of the flotation.

To understand how the flotation fared regarding selectivity, the selectivity index (SI) proposed by Gaudin (1957) was calculated and used as a response value. This index measures the separation of two elements in flotation, and is given by equation 2

$$SI = \sqrt{\frac{R_{1,f} * R_{2,t}}{(100 - R_{1,f}) * (100 - R_{2,t})}} \qquad \text{(Equation 2)}$$

where R denotes the recoveries of both elements 1 and 2, f denotes the floated product and t denotes the flotation tailings (Rey, 2019).

2.3 Factorial design of the experiment

Trials were carried out according to the design of a L8(2^7) orthogonal array (OA), which allows for the study of factor interactions, plus one replication and 4 trials at the centre point, totalling 20 trials. Regarding the study of interactions, the ones included in the design were pH-aeration interaction and pH-collector interaction, which are left unassigned. The trials were conducted at a random order to minimize the effect of noise factors.

The factors and the factorial design are presented in Tables 1 and 2. The *Run* column of Table 2 denotes the order in which the trials were conducted, chosen at random, and it can be noted that the G column was left unassigned in order to add one degree of freedom in the residual's calculation.

Table 2. Factors and their respective OA column

A	pH;
B	Aeration [min]
C	Interaction A-B
D	Collector [g/t/%Zn];
E	Interaction A-D
F	Activator [g/t];
G	-

Table 3. Factorial design of the experiment

	Trial	Run	A	B	C	D	E	F	G
L8	1	19	9	0	-	1	-	200	-
	2	10	9	0	-	2	-	500	-
	3	18	9	30	-	1	-	500	-
	4	13	9	30	-	2	-	200	-
	5	5	12	0	-	1	-	200	-
	6	11	12	0	-	2	-	500	-
	7	8	12	30	-	1	-	500	-
	8	15	12	30	-	2	-	200	-
L8*	9	2	9	0	-	1	-	200	-
	10	14	9	0	-	2	-	500	-
	11	20	9	30	-	1	-	500	-
	12	3	9	30	-	2	-	200	-
	13	6	12	0	-	1	-	200	-
	14	12	12	0	-	2	-	500	-
	15	9	12	30	-	1	-	500	-
	16	1	12	30	-	2	-	200	-
Centre Points	17	16	10.5	15	-	1.5	-	350	-
	18	7	10.5	15	-	1.5	-	350	-
	19	4	10.5	15	-	1.5	-	350	-
	20	17	10.5	15	-	1.5	-	350	-

3. Results and discussion

Through x-ray spectroscopy, the grades of Zn, As and Cu were determined, and it was found that across all trials, Zn and Cu grade increased, while As grade decreased. After calculating the average grade, the enriching ratio was calculated in order to provide a general analysis of the study, presented in Table 4. Table 5 shows the average recoveries by element. In table 6, the selectivity indexes between Zn-As and Zn-Cu are presented, even though selectivity between Zn-Cu was not a part of the factorial design responses, it was an interesting parameter to calculate.

Table 4. Average grade results and enrichment ratio for each analysed element

Element	Sample grade (%)	Average flotation grade (%)	Average enrichment ratio
Zn	4,04	10.13	2,51
As	16.24	16.08	0,99
Cu	0,17	0.59	3,43

Table 5. Average recovery for each analysed element

Element	Average Recovery (%)
Zn	61.42
As	25.58
Cu	84.46

Table 6. Average selectivity indexes between Zn and the other elements

	Average SI
SI Zn-As	2.28
SI Zn-Cu	0.51

Table 7 shows a summary of the worst and best results by trial. By cross referencing Table 7 with each trial's conditions as presented in the orthogonal array, it was possible to see some patterns emerge even before the ANOVA was conducted, such as a possible correlation between Zn and Cu flotation, and that the best trials considering the objective of Zn flotation while depressing As were achieved in trials 3 and 11 which share the same operating conditions.

Table 7. Summary of the better and worse trial results

		Trials max	Trials min
Grade	Zn	3, 11	13, 16
	As	7, 18	3, 11
	Cu	3, 11	14, 16
Recovery	R Zn	7, 19	1, 10
	R As	7, 16	3, 11
	R Cu	5, 15	1, 10
SI	Zn/As	4, 11	6, 13
	Zn/Cu	3, 12	5, 8

Regarding the responses included in the factorial design, it was possible to check for significant curvature in each of them, and It was found that significant curvature was present in the Zn recovery and SI responses.

Through analysis of variance (ANOVA) it was also possible to discover the significant factors for each response values. It was noted pH and aeration were the significant factors across all response. Also, in the recovery of arsenic and the SI, in which the collector dosage alongside pH-aeration interaction were significant factors as well. The studied interactions were not found to be significant factors.

Table 8. Significant factors for each response

R Zn	pH	Aeration	-	
R As	pH	Aeration	pH-Aeration interacion	Colector
R Cu	pH	Aeration	-	
SI Zn As	pH	Aeration	pH-Aeration interacion	Colector

the recoveries of As and Cu was the response factors that didn't show signs of curvature, and it was possible to obtain a linear regression model each that describes their behaviour in the design space (equation 1 and 2)

$$R\ As = -17.87 + 3.51 * pH - 0.58 * Arejamento + 3.76 * Colector + 0.6 * pH * Arejamento \quad (1)$$

$$R\ Cu = +23{,}75 + 5{,}31 * pH + 0{,}27 * Arejamento \quad (2)$$

4. Conclusions

The scope of this work was the flotation of zinc form copper flotation tailings with high arsenic content.

The planning of the trials was done according to a factorial design using Taguchi's orthogonal arrays, which allow for the study of interactions between variables and to reduce the number of total trials needed in order to get the full range of the response in the design space.

Across all trials it was possible to increase the grade of Zn and Cu, while decreasing As. Average recoveries were 62.42% Zn and 25.52% As. The highest recovery achieved was 84.46% in Cu, but its grade was nonetheless considerably low, with its average value being 0.79%. However, in the future, special car should be taken to ensure a better recovery of Zn, instead of Cu.

The results show that the applied methodology was effective in identifying the significant factors that influence each metal's recovery and the selectivity index between Zn and As.

Using linear regression, a model explaining As and Cu recovery in the design space was achieved. The other responses were unable to be modelled due to curvature. The existence of curvature requires the expansion of the experimental plan, i.e. conducting more trials, in order to estimate the higher order terms.

4.1 Future works

As already mentioned, future works must include the expansion of the factorial design in order to estimate the higher order terms in the responses that showed significant curvature.

The study of flotation kinetics with the material used might provide relevant data about the behaviour of the particles in a flotation system, allowing for the optimization of flotation time.

The trials conducted were all direct flotation trials, where the floated product is the product that is concentrated, and the sunken product is considered tailings. However, reverse flotation is also an option, tweaking the operating conditions with the objective of sphalerite depression, namely at a low pH.

The reagents used were adequate to the objective of the work, however, there are several reagents which's study might also garner favourable results, such as the use of $Ca(ClO)_2$, SH and H_2O_2 as depressants for As.

If more trials are conducted, it might be suited to investigate a wider range of elements in the material, as, for example the presence of Fe might indicate a different approach to the operating conditions should be investigated.

If satisfactory results are achieved, then a full economic feasibility study should be conducted, in order to investigate the possibility of implementing a zinc processing unit, taking into account all costs of equipment, labour, reagents, and the price of Zn concentrate.

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