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Environmental remediation of sulfidic tailings with froth flotation: reducing the consumption of additional resources by optimization of conditioning parameters and water recycling

Ted Nuorivaara[a], Anna Björkqvist[a], John Bacher[b] and Rodrigo Serna-Guerrero[a]*

[a]Aalto University, Department of Chemical and Metallurgical Engineering, Vuorimiehentie 2, 02150 Espoo, Finland

[b]VTT Technical Research Center of Finland Ltd., Biologinkuja 7, 02150 Espoo, Finland

*Corresponding author: rodrigo.serna@aalto.fi, +358 50 4637 800

Abstract

The removal of sulfidic species in tailings using froth flotation is a promising approach to prevent phenomena such as acid mine drainage. However, flotation requires the consumption of reagents and water that represent additional expenses. Despite the strong interest of scientists and industry alike on tailings remediation, there is no study on the minimization of resource consumption to promote the implementation of desulfurization with froth flotation. Following a systematic analysis based on Design of Experiments (DoE), this work aims to determine the implications of a decrease in the consumption of flotation reagents and fresh water.

It was found that: i) recovery of sulfidic species is strongly influenced by collector concentration and the use of a preliminary re-dispersion step; ii) higher frother concentrations have a negative impact on sulfur grade in the concentrate; and iii) the interactions between the conditioning variables hereby explored have no significant impact on flotation performance. Composition analysis showed that flotation further aids in the removal of hazardous species, such as As, Co and Zn. Finally, the use of recycled water appears possible since flotation performance remained unchanged over 10 flotation cycles, despite the observed accumulation of metallic ions and organic species in the process water.

Keywords: Acid mine drainage; flotation; tailings; water recirculation; mining waste remediation

1. Introduction

One of the most relevant environmental concerns currently faced by the mining industry is the so-called acid mine drainage (AMD). This phenomenon is caused by the oxidation of sulfur-containing minerals, which often are generated as tailings, resulting in acidification of tailings ponds. The acidic conditions in tailings ponds have been associated to severe environmental hazards, including the dissolution of hazardous metallic species, such as As, Cd, Co, Cr, Cu, Pb, Ni, Zn and V [1] along with their migration into the surrounding ecosystems [2]. Consequently, numerous studies have been made to find procedures which would inhibit or restrain AMD [3-9]. As every mine has their own unique geological and environmental conditions, the formation of AMD is also unique for each site [10]. In 2006, the EU waste directive No. 2006/21/EC was issued, stating that mine waste must be characterized in order to prevent or inhibit its negative impact on the environment, landscape and public health.

AMD is a well-acknowledged issue in the processing of sulfidic Cu, which is typically associated with other minerals such as pyrite or sphalerite. As the commercial value of Fe is lower than that of Cu, pyrite is usually depressed during e.g. Cu and Zn flotation, reporting finally to the tailings. However, pyrite and pyrrhotite are among the most common species responsible for AMD due to their abundance and tendency to oxidize readily [11], according to the following general reaction:

$$FeS_2(s) + \frac{15}{4}O_2(aq) + \frac{7}{2}H_2O \rightleftharpoons Fe(OH)_3(s) + 2SO_4{}^{2-}(aq) + 4H^+(aq) \qquad (1)$$

The oxidation of pyrite is a slow process if it is covered with water or other inhibiting layers. Additionally the thickness of the tailings is a relevant measure in the oxidation process, with thicker heaps associated with slower oxidation. For that reason, some researchers have proposed the use of physical barriers to inhibit the oxidation responsible for AMD, e.g. fly-ash and sludge layers [12,13] or natural soil [6].

Flotation is an option that has recently called the attention to reduce the environmental impact of sulfide-bearing tailings [3,7-9,11] . Froth flotation is a well-known unit operation in the mineral processing field, and some studies have claimed that it can be used to separate species responsible for AMD from tailings to make them useful in other low impact applications, such as backfill paste for underground mines [4]. Alternatively, fractions obtained via flotation can also be used as an inhibiting layer for sulfide-rich fraction in tailings ponds, possibly reducing the neutralization costs [14]. The promise of lower environmental impact of tailings can also help in obtaining a license to operate in both new and established mining operations [15]. While these studies have showed that environmental desulfurization via flotation is a viable option, none of them address the need of additional resources or provide strategies to minimize them.

Indeed, the application of flotation as treatment for tailings may be limited by its need for additional resources, such as energy, water and chemical reagents. Regarding the latter, a typical flotation plant requires a variety of reagents whose aim and composition affect directly the separation performance. Reagents that render the desired mineral surfaces hydrophobic are needed to promote the bubble particle attachment of desired minerals. For this purpose activators and collectors are necessary. Activator adsorption on sulfide minerals and the subsequent xanthate adsorption to the activated mineral surface have been extensively studied [16-20]. With respect to tailings desulfurization, the most common approach is the activation of pyrite with Cu following two subsequent steps [20]:

1) Cu^{2+} reduction to Cu^+ by the oxidation of S^{2-} to S^-
2) Fe^{2+} oxidation to Fe^{3+} by the reduction of S^- to S^{2-}

These steps result in the formation of a $CuFeS_2$ layer on the surface of pyrite that can readily react with sulfur-containing collectors. After the activation of pyrite, the xanthate collector adsorbs onto the activated mineral surface, predominantly forming dixanthogen species while metal-xanthates are present as minor adsorbates [19], effectively rendering pyrite surfaces hydrophobic.

Although previous works have identified a positive impact of collector concertation on recovery [3,21], no attention has been paid to the influence and potential interaction with other conditioning parameters, e.g. frother concentration. Frothers are used to control the bubble size and the froth stability of the system. It has been shown that flotation is most efficient when working with as small bubbles as possible thus operating in conditions above the critical coalescence concentration is important. While the presence of frothers improves recovery, it is well documented that its excess promotes the entrainment of unwanted gangue minerals [22,23].

With respect to the consumption of water, froth flotation is a water-intensive operation and the use of suitable water management strategies has gained importance in recent years [24]. Furthermore, environmental concerns revolve around the detrimental impact on water quality when a watershed is extensively used for mining operations. In big mining regions, such as North America, Australia, Chile, and South Africa, sites are often in water shortage areas [25] and water recycling in mining and minerals processing is becoming mandatory. Along with declining ore grades, the need to extract and process increasing amounts of ore demands larger volumes of process water. Water recycling is therefore necessary and is a practice that is becoming widely implemented. A proper water recycling system not only decreases the need of fresh water, it also results in lower discharge volumes into the environment and may reduce the consumption of reagents retained within the water circuit. However, recycling introduces quality irregularities in the water, which can influence the process in unexpected and uncontrolled manners [26]. One such problem is the dissolution of metallic species in process waters which can also influence the performance of concentrator plants, although some authors are currently looking for methods to extract valuables from process waters with, e.g., the use of polymeric membranes [27].

Considering that the idea of water recycling in mining operations is attractive from the point of view of efficient resource management, various studies regarding the impact of recycled water quality on flotation performance for various minerals and different water compositions can be found in the literature. As an example, some recent publications related to sulfidic ores and their key findings are compiled in Table 1. As seen, these studies present some conflicting results regarding the impact of recycled water on the recovery of sulfidic ores. Therefore, it is necessary to explore the influence of water recirculation aimed specifically at the remediation of tailings since such information is not yet available (to the best of the authors' knowledge).

Table 1. *Compilation of water quality studies in recent years*

Ore Type	**Water Origin**	**Studied species**	**Effects/ accumulation**	**Reference**
Copper-gold ore, precious metals	Tailings thickener overflow and tailings facilities	TDS[1]	Growing TDS levels in recycled water over a long observation period	[28]
Copper-gold-silver ore	Tailings thickener overflow	Xanthate, IPETC[2]	The recycled water contained IPETC in significant concentrations while xanthate was undetectable	[28]
Platinum group metals	Tap water, thickener waters and sewage effluent	TDS[1], TSS[3] and conductivity	Lower recovery and higher grade was achieved using recycled water	[29]
Galena, chalcopyrite, sphalerite, pyrrothite	Simulated tailings dam water	Cu^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, xanthate	Higher grade and selectivity of galena can be achieved using recycled water	[30]
Chalcopyrite, galena and sphalerite	Simulated water, process water	SO_4^{2-} and Ca^{2+}	Better recoveries with process water compared to tap water	[31]

[1] Total Dissolved Solids
[2] Isopropyl Ethyl Thiocarbamate
[3] Total Suspended Solids

For the reasons mentioned above, the work hereby presented has two specific goals: i) the study of the influence of conditioning parameters (i.e., collector and frother concentration and re-dispersion during conditioning) on the desulfurization of tailings using response models obtained through Design of Experiments (DoE), and ii) investigating whether such treatment can be conducted using recycled water. In this manner, the present work aims at identifying strategies to minimize the environmental impact of sulfidic tailings without the extensive consumption of additional resources. As will be presented later in this article, the main contributors in terms of conditioning parameters were collector concentration and re-dispersion during conditioning, while water recirculation demonstrated minimal effects on flotation performance.

2. Materials and methods

2.1 Materials

The mineral samples used in this study were tailings from Pyhäsalmi mine (First Quantum Minerals Ltd.) in Finland. The main characteristics of the tailings are presented in Table 2. A detailed mineralogical study conducted by the Geological Survey of Finland [32] is presented in the Supplementary Information (S1). The tailings hereby studied present a high composition of pyrite since Pyhäsalmi mine operated for several decades without a pyrite flotation circuit and its operation is intermittent. Briefly, tailings in Pyhäsalmi mine are produced as a combination of rejected minerals from the sequential flotation of chalcopyrite, sphalerite and pyrite. Although it is difficult to determine the exact age of the tailings, the samples used in this study were estimated to have stayed in the tailings pond for several years. Because of this, it is likely that the surfaces of the tailings are tarnished or coated with a layer of fines which have settled onto the minerals during their time on the bottom of the tailings pond. After collection, the tailings samples for this study were freeze-dried to prevent further oxidization. Dry agglomerates were crushed and passed through a 500 µm sieve and then separated by quartering and divided with a Fritsch Rotary Sample Divider to samples of approximately 500 grams.

Table 2. Characteristics of the Pyhäsalmi tailings used in this study

Main elements*	**Fraction (%)**	**Particle size**	**mm**
Fe	28	d50	35
S	22	d80	120
Si	7.05		
Ca	5.01		
Ba	3.02	**Acid potential**	
Mg	2.05	NP[1]	1.18
Al	2.03	AP[2]	17.69
Na	0.54	NPR[3]	0.07
K	0.39		
Zn	0.24		
Mn	0.12		
Ti	0.11		
Cu	0.1		
As	0.06		
P	0.04		

* Composition measured with XRF
1 Neutralization Potential
2 Acid Potential
3 Neutralization Potential Ratio

The flotation experiments were performed using deionized water. The collector used in this study was an industrial grade sodium iso-butyl xanthate (SIBX). The frother was NasFroth 350 (NF350), a mixture of polypropylene glycol ethers supplied by Nasaco International LLC. The activator was $CuSO_4 \cdot 5H_2O$ from Honeywell International, Inc. These reagents were chosen because they represent a typical chemical system used in desulfurization flotation, where pyrite is activated by using copper sulfate, the collector is a relatively long chained xanthate collector and a polyglycol ether is used as the frother [9,11,21].

2.2 Methods

2.2.1 Optimization of sulfidic tailings flotation

Since flotation has already been proven to be an economically attractive method to manage tailings in certain scenarios [21], the goal of the first part of this study was to find optimal conditioning parameters to separate sulfidic minerals from the tailings. Due to the complex nature of flotation, a factorial DoE was used to observe the influence of different reagent dosages. The chosen concentration levels were based on preliminary flotation tests not shown here, and are well within the range reported in other works dealing with flotation of sulfidic tailings [21]. It is worth noting that some studies used lower collector concentrations [3], but their pyrite grades are also significantly lower. For the sake of clarity, in the present work we refer to the untreated tailings as "*feed*", while the minerals reported in the froth fraction are referred to as "*concentrate*" and "*tailings*" for the fraction remaining in the flotation cell after processing.

Flotation was carried out in an Outotec 1.5 l laboratory-scale cell. Table 3 shows the experimental conditions used according to the factorial DoE. The variables explored were collector concentration, frother concentration and whether a preliminary re-dispersion step is applied before addition of reagents. The preliminary stirring was performed with the aim to disperse any fine solids deposited on the pyrite surfaces. This step also helped to evaluate whether a more energy intensive unit operation to increase the effective surface area of the sulfide minerals (e.g., re-grinding) can be avoided. If stirring was included in an experiment, it was conducted according to the parameters presented in Table 4. The order of experiments was randomized, and experiments 9-11 were replicates to provide information on the curvature of the factor effects, as well as experimental error.

Table 3. *Experimental parameters of flotation experiments*

Experiment number	Order of experiments	Frother dosage (ppm)	Collector dosage (g/t)	Stirring
1	1	12	30	ON
2	4	30	30	ON
3	9	12	100	ON
4	11	30	100	ON
5	8	12	30	OFF
6	7	30	30	OFF
7	10	12	100	OFF
8	3	30	100	OFF
9	2	21	65	ON
10	5	21	65	ON
11	6	21	65	ON

Table 4. *Parameters of preliminary stirring stage*

Parameter	Value
Impeller speed	1300 rpm

Conditioning time	10 min
Solid content	50 w-%
Mass of solids	600 g
Mass of water	600 g

The detailed description regarding the conduction of the flotation tests is presented in the Supplementary Information (S2). All flotation experiments were carried out using experimental parameters presented in Table 5. Each fraction collected throughout the flotation experiments was dewatered by filtration and completely dried in a natural convection oven at a temperature of 40 °C.

Table 5. *Operating parameters used in flotation experiments*

Parameter	**Value**
Activator concentration ($CuSO_4$)	200 g/t
Air flow rate	4 l/min
Impeller speed	1300 rpm
Flotation time	30 min
Initial solid content	33 w-%
Initial mass of solids	600 g
Total volume of suspension	1.5 l

The results were analyzed with the help of a factorial design software (MODDE™) to create a partial least squares model to predict the performance of the experiments in terms of mass pull, sulfur recovery, sulfur grade in the froth and sulfur grade in the tailings.

Finally, as described in detail in the Supplementary Information (S3), characterization on neutralization potential ratio (NPR) and chemical composition of concentrate and tailings were carried out.

2.2.2 Flotation with water recirculation

The second part of the study consisted of a flotation series with water recycling, an aspect of key importance for the future of the industry [24]. For the first flotation cycle, deionized water was used. The process water collected after each flotation cycle was then reused in the subsequent experiment. The operating conditions were the same as in Section 2.2.1, using the reagent dosages from Experiment 3. As will be presented in the Results section, these conditions were considered the most attractive. Since the flotation conditions were chosen based on the optimization results, this also represents a validation set for the response model obtained by DoE. After each flotation step, the concentrate and tailings slurries were separately filtered through a 0.45 μm paper. The filtrates were combined and this mixture was used in the following flotation test. For clarity, a flowchart of one complete test cycle can be seen in Figure 2. The composition of the solids, as well as the quality of the water was studied after each flotation step.

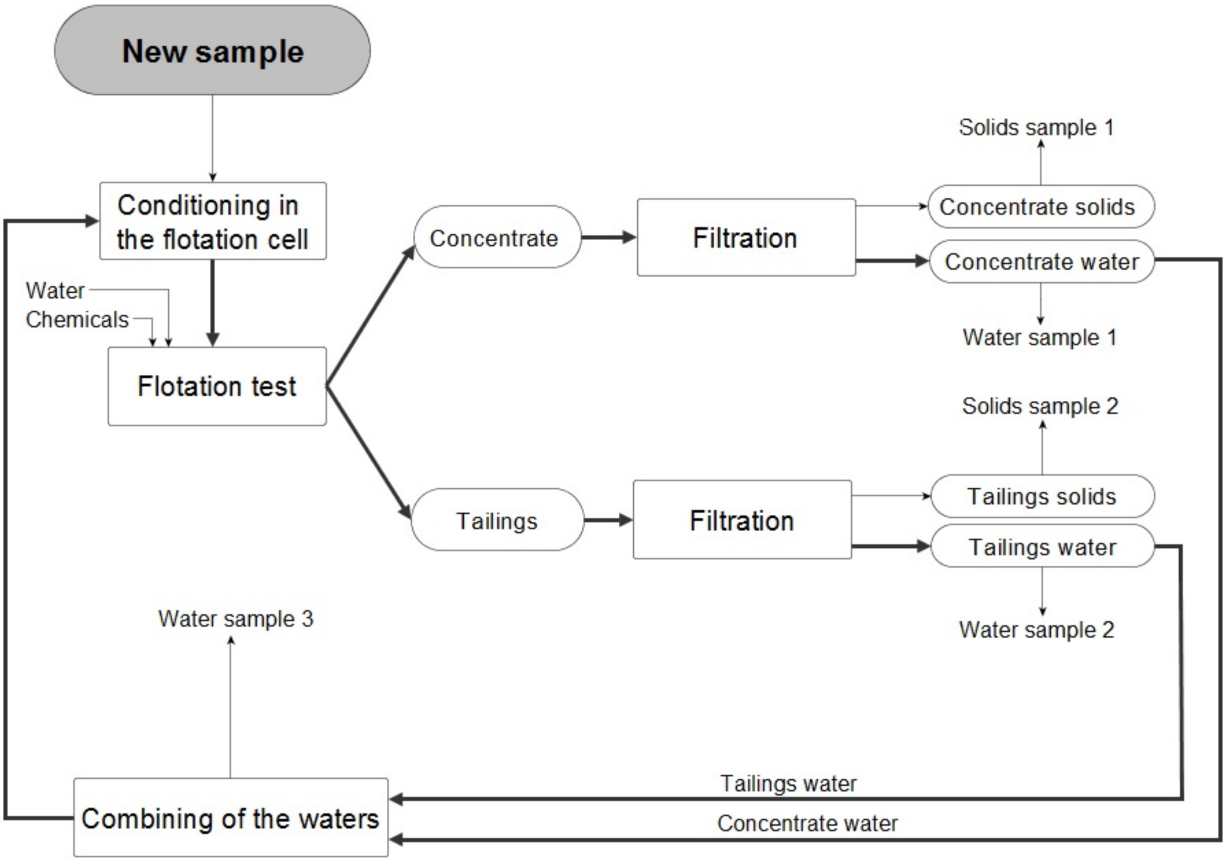

Figure 2: *Flowchart of experimental work for the treatment of tailings with water recycling*

Since sampling and handling reduced the amount of process water recovered, additional deionized water was introduced to the process at each flotation step to maintain a constant pulp level. The relative amount of recycled water was recorded during every cycle (Table 6).

Table 6. *Proportion of recycled water (%) at each flotation cycle*

Cycle	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Recycled water (%)	0	70.4	65.2	66.1	63.0	71.2	74.2	60.6	67.3	70.4

3. Results and discussion

3.1 Removal of sulfides

As mentioned in the previous Sections, the first part of this study is centered around the impact of conditioning parameters on the removal of sulfidic species without water recirculation. The optimized parameters were subsequently used in experiments with water recirculation.

3.1.1 Optimization of sulfidic tailings flotation

The sulfur recovery and grade results obtained after 30 min of flotation are displayed in Table 7. As seen, a broad range of recovery values was obtained, from 30 to 92 %. This further justifies the levels chosen for the DoE, as they provide a wide perspective on the influence of these conditioning parameters. The first clear finding from Table 7 is that the preliminary stirring (experiments 1-4 and 9-11) enhanced the flotation performance in terms of mass pull and sulfur recovery. A good example on the advantage of preliminary stirring can be found by comparing Experiment 8 and Experiments 9-11. While there was a higher dosage of reagents in the former (*Table 3*), the recovery and grades were similar to that of experiments 9-11. Comparing to similar conditioning methods reported [33,34], the preliminary stirring used in this study improved the flotation performance without the need to change the impeller, the container or to use extremely high revolutions per minute. An additional difference was that in this study the reagents were introduced after a separate stirring step. Thus representing a simple and a resource-effective conditioning procedure.

As discussed in Section 2.2, it is not uncommon that minerals are coated by fine particles or slime preventing the efficient reaction of sulfidic species with activators and collectors. Indeed, the results in Table 7 show that sulfur recovery is consistently lower in experiments where the preliminary stirring stage was not applied. These findings suggest that liberation using an energy intensive re-grinding step [4] could be avoided and a less energy consuming re-dispersion step suffices to promote efficient flotation. Admittedly, this may only be possible provided that the pyrite in the tailings have a sufficiently large grain size to be significantly liberated, as is expected from the tailings used in this study [32].

***Table 7.** Sulfur results of the flotation experiments*

Experiment number	Mass pull at 30 min (%)	Sulfur recovery at 30 min (%)	Sulfur grade in the froth fraction at 30 min (%)	Sulfur grade in tailings (%)
1	20.5	32.8	42.0	22.2
2	31.3	48.1	40.0	19.6
3	49.2	81.1	46.3	10.4
4	53.4	91.6	45.5	4.8
5	19.8	30.2	39.5	22.5
6	28.3	41.9	41.0	22.4
7	42.7	72.3	47.2	13.5
8	47.5	80.4	43.2	9.6
9	47.1	77.6	43.6	11.2
10	48.5	80.8	43.4	9.7
11	50.3	80.4	41.8	10.3

An interesting observation is that the pre-stirring had only a modest effect on the grade of sulfur in the froth fraction. Additionally, the grade of sulfur in the froth was generally higher with smaller frother dosage (e.g., Experiment 3 vs. Experiment 4). This behavior is likely associated to the generally accepted trend that a more stable froth increases recovery at the expense of grade [35]. This is a point to keep in consideration if the sulfur grade of the product is of interest.

Finally, the highest recovery of sulfur was obtained in Experiment 4. With these parameters, a sulfur recovery of over 90 % was measured, while the sulfur content in the tailings decreased to less than 5 %. Interestingly, these results are well in line with studies conducted on Canadian tailings aimed at the optimization of operating conditions [11], which indicates that similar results may be obtained for other sulfidic tailings although each tailings are expected to present unique mineralogy.

Based on the results of the DoE, a response model was created with MODDE™ to further analyze single and combined effects of the varied experimental conditions. Details of the linear model can be found in the supplementary information (S4).

Due to the nature of flotation and the amount of experiments in the design, some variation on the results and accuracy limitations of the model are expected (Figure S2). Nonetheless, the model can be used to generate response surfaces to visualize and predict performance within the scope of reagent dosages used in this study. Figures 3 and 4 show response surfaces for sulfur recovery and sulfur grade in froth, respectively. Mass pull and sulfur grade in tailings strongly followed the tendency of sulfur recovery and thus are not presented.

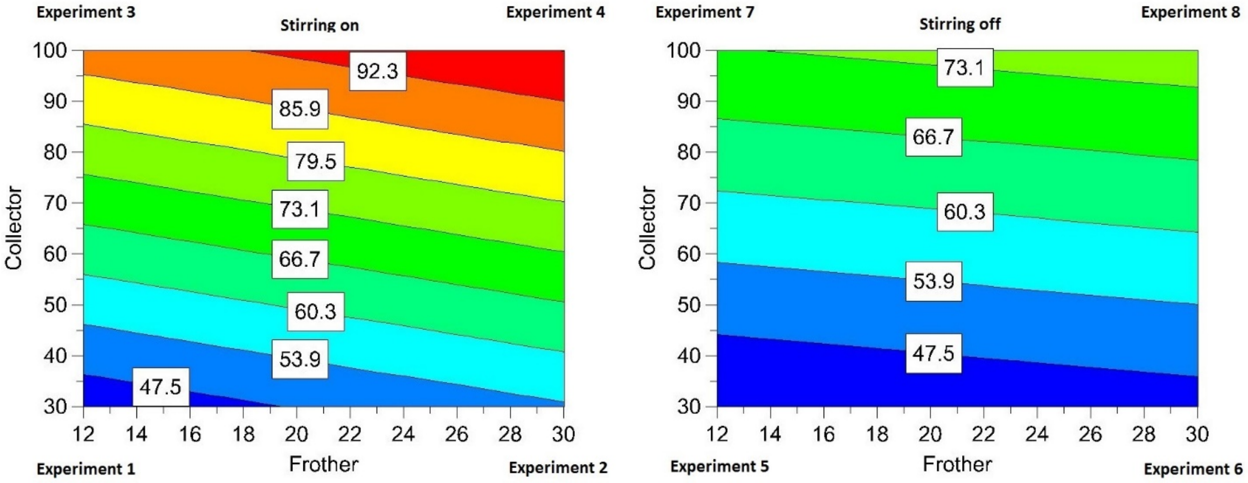

Figure 3. *Combined effects of variable parameters on sulfur recovery (collector and frother concentration in g/ton and ppm, respectively)*

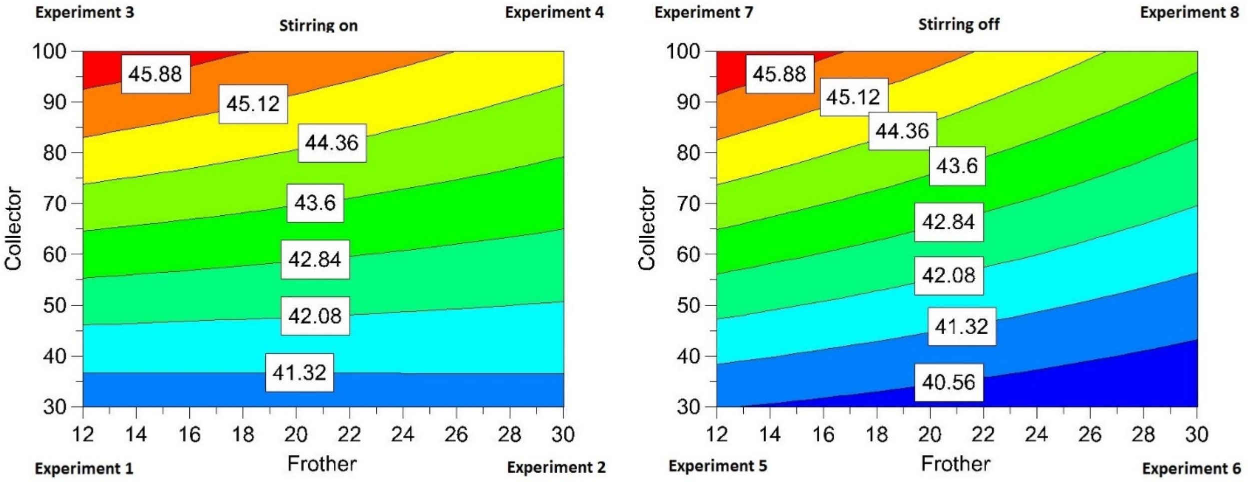

Figure 4. *Combined effects of variable parameters on sulfur grade in the froth (collector and frother concentration in g/ton and ppm, respectively)*

The illustrations can be used to predict outcomes of similar experiments and optimize reagent dosages to match a desired outcome. As seen in Figure 4, the optimization of recovery is rather simple since its maximum value is located at the upper limits of the reagent dosages, in line with results previously reported by other groups [3,21]. Initially, this may not seem like a positive finding as it suggests that higher recoveries are obtained at the expense of higher reagent dosages. Nevertheless, Figure 4 also shows that the use of preliminary stirring had a positive impact on recovery, with up to 15 % higher recovery compared to their non-preconditioned counterpart. Thus, flotation performance can be enhanced by using preliminary stirring rather than consuming excessive amounts of collector.

Another interesting observation from Figure 4 is that the sulfur grade in the froth fraction is not directly proportional to the addition of frother. In fact, the sulfur grades appear to be negatively affected by higher frother concentrations, particularly at the upper limit of collector concentration. Since recovery is not much affected by frother concentration, this observation further supports the explanation that increased frother concentration promotes the non-selective entrainment of particles [22,23,33]. This suggests that the use of additional resources in the form of excess frother amounts should in fact be avoided. It is also seen that preliminary stirring does not have a significant impact on the grade of sulfur in the froth. A reasonable interpretation of these results is that the re-dispersion step does not promote the activation of new species.

As detailed in the Supplementary Information (S4: Figures S3 and S4), the sensitivity analysis of the regression model helps to determine which are the statistically relevant factors for sulfur recovery and grade. For the former, only collector dosage and stirring can be considered influential. Regarding sulfur grade, only collector dosage is statistically relevant. According to the statistical analysis, frother concentration has a slightly positive impact on recovery and a negative one on grade, although its influence is too small to be considered of real statistical relevance. As the results presented in Figures 3 and 4 are consistent with these proportionalities, perhaps it is necessary to carry out an analysis with a larger number of experiments to decrease the calculated error. A further interesting finding is that no synergistic effect of conditioning parameters can be claimed, as none of the combined effects of variables are above the minimum level of statistical relevance (Figures S3 and S4).

Since collector concentration is the most influential parameter, it was decided to study its impact on flotation kinetics. The first-order kinetic constants for Experiments 2 and 4 were determined to have similar values, i.e., 2.54×10^{-1} and 2.69×10^{-1} min^{-1}, respectively (see Supplementary Information, S5). Therefore, it can be said that the use of lower collector concentrations is not a limiting factor regarding flotation kinetics. Nevertheless, the total recovery of sulfur inevitably correlates to the total surface area that has been hydrophobized and this is stimulated by a higher collector dosage.

3.1.2 Impact on environmental properties

Three properties were studied in terms of environmental impact of the samples: acid producing potential, the amount of contaminating solids and the amount of contaminating dissolved species. The NPR value of the analyzed froth fraction (i.e., 0.00) had a clearly higher acid producing potential compared to the feed or the tailings (i.e., 0.07 and 0.77, respectively). As detailed in the Supplementary Information (Table S5), the carbonate coal was enriched into the tailings fraction but its concentration was too small to sufficiently increase its NPR value beyond the acid producing zone. Thus, the NPR value of the tailings is still regarded as acid producing, although compared to the NPR value of the feed, there is a clear improvement. According to a previous study on the tailings of Pyhäsalmi mine [36] it is possible to further increase the NPR-value by using a multi-stage grinding and flotation, which would consequently increase the energy and resource intensity of the process and thus was not pursued in this study.

In order to determine the environmental impact of the flotation products, the limits specified for contaminating species by the Finnish government Decree on the Assessment of Soil Contamination and Remediation Needs

(214/2007) were used as benchmark [1]. A detailed comparison between the threshold levels established in the Decree and the results of Experiment 4 are presented in the Supplementary information (S6).

The results presented in Table S6 show that the species exceeding the higher guideline value (As, Cu & Zn) do so in both the tailings and the froth fraction. Thus, flotation does not sufficiently improve the environmental properties of the tailings to comply with these regulations. Nonetheless, species such as As, Co and Zn were enriched into the froth fraction, demonstrating the potential of flotation for tailings remediation. The results are well in line with results of previous studies [7-9], where the major sulfidic metal minerals reported to the froth fraction. On the other hand, a noteworthy phenomenon is the enrichment of species that represent the minority group of sulfide minerals into the tailings, such as Pb, Ni and V, reflecting the results reported in a recent study by Lutandula and Maloba [37]. This may prove to be a problematic scenario as Pb concentration in the tailings exceeded the threshold value of the Finnish government Decree (214/2007). Therefore, it is important to thoroughly characterize the properties of the remaining tailings in order to avoid accidental promotion of certain toxic species after flotation. The above-mentioned results indicate that a different approach, e.g., leaching, may be needed for the removal of the remaining heavy metals.

In Finland, there are currently no regulations regarding the leaching criteria of mine waste. Thus, the results of Experiment 4 were compared to the Finnish Government Decree on Landfills (331/2013). This comparison can be used as a guideline in studying the environmental properties of the samples regarding dissolution of species. The comparison between the threshold values from the Decree on Landfills and the standardized leaching test (S3) for experiment 4 (EN 12457-2) is presented in Table S7.

According to the best knowledge of the authors, such comparison between desulfurized mine tailings and leaching criteria of landfills has not been studied before. Yet the results show valuable information regarding the possibility of obtaining a waste fraction from mining processes that could be directly used as landfill. As seen in Table S7, the tailings used as feed are already suitable to be landfilled as inert waste with respect to most species. The only species exceeding the threshold for inert waste are Ni, Zn and sulfate, while the fluoride level is at the threshold value. After flotation, the Ni concentration was reduced below the threshold of inert waste, the amount of dissolved Zn was almost halved and the amount of dissolved sulfates decreased, although in the latter two cases the reduction was not below the threshold for landfill waste. Overall, it can be said that the environmental properties of tailings were improved after the flotation treatment hereby reported, although in specific cases further treatment may be required.

3.2 Flotation with water recirculation

Based on the results in Section 3.1, the parameters of Experiment 3 were chosen for flotation studies with water recirculation. This experiment used pre-stirring and the higher level of collector concentration associated with high recovery. Additionally, the lower frother concentration was used, which had a low impact in recovery while favoring the grade of the sulfur in the product. The subsequent step was to investigate whether flotation could be performed using recycled water and to identify potential limitations of such practice. The evolution of recycled water quality throughout 10 cycles of flotation experiments and its impact on flotation performance was studied.

3.2.1 Evolution of water quality

Although pH was uncontrolled in these experiments, only minor variations throughout the study were observed, with values fluctuating between 5.3-5.55. Alternatively, conductivity values accumulated throughout the flotation cycles (Figure S6), reflecting the dissolution of various compounds originating from the ore during each cycle.

Table 8: *Concentration of species in recycled water*

		Cycle

Species	Unit	1	2	3	4	5	6	7	8	9	10
SO_4^{2-}	mg/l	3600	4900	6000	6400	7000	7400	8000	7600	7800	8200
S	mg/l	1200	1600	1900	2100	2200	2500	2700	2600	2600	2700
Mg	mg/l	550	970	1200	1300	1400	1600	1700	1700	1700	1800
Ca	mg/l	490	440	430	430	460	450	450	450	450	450
Mn	mg/l	48	81	95	100	110	130	140	140	140	140
Zn	mg/l	27	44	54	59	62	69	77	74	75	77
K	mg/l	24	38	44	48	48	54	58	57	57	59
Na	mg/l	12	20	25	28	28	33	37	36	38	38
TOC[1]	mg/l	7.6	11	13	14	15	17	19	17	18	18
Si	mg/l	3.7	4.9	5.1	5.3	5.2	5.8	6.3	6	5.9	6
Cu	µg/l	310	480	610	620	610	770	870	730	790	880
Fe	µg/l	150	47	550	87	85	320	250	180	150	190

1 Total Organic Carbon

The results of the composition analysis for combined waters can be seen in Table 8. One clear observation is that the concentration of all species increased steadily until the 7th cycle, except for Ca and Fe. Fluctuation in the Fe concentration may be associated with uncontrolled dissolution and precipitation reactions taking place in the flotation cell. It also seems that Ca was saturated during the first flotation cycle, possibly related to highly soluble calcium in the ore. However, the early saturation with Ca did not have a significant effect on the flotation performance.

As suspected, several chemical species accumulated in the water due to recycling. Most species, e.g., Mn, Zn and Fe, probably originated from the tailings sample, while Na may have partially originated from the xanthate. The activator was a source of both copper and sulfate, which were present in relatively high concentrations starting from cycle 1 and accumulated throughout the cycles. Another fraction of the sulfate ions probably proceeds from the tailings. Finally, most of the total organic carbon (TOC) presumably originated from the flotation reagents, as has been previously reported by other authors during reprocessing of tailings [38].

The SIBX concentrations of separate and combined waters are presented in Supplementary Information (Figure S7). There is a clear accumulation of SIBX throughout the whole set of experiments. However, the amount of residual xanthate remained low throughout all experiments due to the effective adsorption of the reagent onto the mineral surfaces and to the xanthate mainly reporting into the concentrate water. As will be detailed in the following section, this accumulation did not have a significant influence in the flotation efficiency of sulfides. It is possible that the amount of accumulated SIBX in these experiments was too low to have an influence in the overall flotation. However, industrial operations may cycle water well over 10 times and, were this trend to continue, it may be possible to further decrease the addition of fresh collector at some point. Indeed, it was recently reported that monitoring and controlling xanthate additions in an industrial process resulted in reduced need of fresh xanthate additions into the process [39].

Although the amount of residual frother was not specifically measured in this study, the TOC results (Figure S8) suggest that frother may have accumulated into the water during the flotation experiments. Indeed, xanthate cannot be the main contributor of TOC, since TOC concentrations were measured in several milligrams per liter and the highest measured xanthate concentration was only approximately 1 mg/l. Assuming that TOC originated mainly from the reagents, frother is the most likely contributor to TOC in the process water. In other words, it seems that frother accumulation took place, but it did not significantly affect the process as will be detailed in the following Section (3.2.2). The latter observation further validates the low impact of frother concentration expected from the results of the statistical analysis discussed in Section 3.1.

3.2.2 Grade and recovery of minerals

The sulfur recovery and grade as well as mass pull of the experiments with water recirculation are presented in Table 9. Based on the relatively small standard deviation in cycle 1, it can be said that the experimental results obtained have an acceptable degree of accuracy.

Table 9: *Recovery and grade of sulfur*

Cycle	Mass pull at 30 min (%)	Sulfur recovery at 30 min (%)	Sulfur grade in the froth fraction at 30 min (%)	Sulfur grade in the tailings (%)
1*	41.4 (0.79)	72.7 (0.61)	44.2 (1.91)	13.4 (0.62)
2	42.4	70.5	43.5	14.2
3	44.3	72.4	40.2	13
4	43.0	73.1	44.9	13.4
5	44.3	75.0	45.2	12.8
6	44.4	75.0	44.9	13.1
7	44.3	74.3	44.1	13.2
8	43.4	74.0	43.4	12.8
9	49.7	83.8	46.6	9.53
10	43.5	73.6	44	13.3

*The values for cycle 1 are the average of three repetitions, with the standard deviation presented in parenthesis

In general, mass pull, recovery and grade remained constant during the experiments, within experimental error. The result of the ninth cycle was higher compared to the other results, however, it can be interpreted as an outlier since the recovery obtained in cycle 10 was of 73.6 %. It is worth noting that, although the experiments with water recirculation were carried out in the same conditions as Experiment 3 (Table 7), there was a difference between the recovery of the experiments with fresh and with recycled water. Taking into consideration that all three experiments corresponding to cycle 1 (Table 9) reported consistent recovery values, this discrepancy cannot be attributed to either experimental error or to the use of recycled water. A more feasible explanation may lie with the heterogeneity and age of the feed mineral. The samples were stored dry at room temperature, but a few months elapsed between the experiments in Section 3.1 and those in the present Section. Therefore, some chemical changes at the mineral surface during that period cannot be discarded. It is thus possible that the samples for the DoE and those for water recycling experiments had slightly different characteristics. Nevertheless, it should be kept in mind that the main purpose of the second part of this work was not simply to measure recovery, but rather to evaluate changes in flotation performance as water is recycled.

The main finding was that pyrite flotation from tailings appear to be unaffected by the use of recycled water, at least with the experimental conditions hereby studied. Both recovery and grade remained stable throughout 10 flotation cycles. According to the XRF results (Table S8), the concentrate contained similar grades of S and Fe after the first and last cycle, which indicates that flotation efficiency for pyrite remained nearly unchanged. This results are particularly interesting since the presence of specific ionic (e.g., sulfate and calcium) species have been considered positive towards pyrite flotation [40]. However such correlation cannot be made in this study.

4. Conclusions

As stricter regulations and a deeper environmental awareness become widespread, it is likely that desulfurization of tailings will become universally implemented in mining operations. In this study, a few strategies to optimize the performance of flotation of sulfidic tailings by decreasing the consumption of flotation regents and fresh water were identified. While admittedly the results of this study cannot be universally applied to every system, the following findings may provide a starting point to promote the implementation of froth flotation for tailings remediation:

1. By adding a preliminary re-dispersion step, the recovery of sulfidic components can be significantly enhanced, which could be translated into lower consumption of reagents, particularly collector. A pre-dispersion stage seems to be sufficient to obtain high recoveries and no re-grinding seems to be needed. Furthermore, reducing frother dosage increased the sulfur grade in the froth fraction, at least within the studied concentrations.

2. The use of flotation also resulted in an improvement of the environmental properties of the tailings in terms of increased NPR-value, reduced concentrations of toxic heavy metals such as As, Co and Zn as well as significant reductions in leaching properties in terms of Ni and Zn.

3. It was demonstrated that the desulfurization of these particular tailings by froth flotation is possible with recycled process water. The flotation efficiency of sulfidic groups, mostly consisting of pyrite, was not significantly inhibited throughout 10 cycles.

4. Combining the findings of this study opens the possibility to apply the flotation approach for tailings remediation even in sites where water scarcity is an issue while using a limited amount of additional reagents.

Finally, none of the studied conditions seemed capable of reducing the collector dosage without affecting the recovery. It is possible that new flotation chemistries could hold the answer for further reductions in the overall reagent consumption.

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