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Optimization of Titanium Recovery from Tin Tailings Using Flotation Route

S. Subandrio [1], W. Dahani [1,*], R. Sundari [2,*], R. Kurniawati [1], I. Marwanza [1] and F. S. Darren[1]

[1]Department of Mining Engineering, Faculty of Earth Technology and Energy, Universitas Trisakti, Grogol Petamburan, Jakarta 11440, Indonesia
[2]Department of Mechanical Engineering, Universitas Mercu Buana, Meruya Selatan, Jakarta 11650, Indonesia
*Corresponding Authors: wiwik_d@trisakti.ac.id (WD); rita.sundari@mecubuana.ac.id (RS)

Abstract

Titanium has found widespread application across various industries due to its high corrosion resistance. It is commonly used in dental equipment, surgical instruments, bone implants, and marine components, and serves as an engine material in high-temperature environments. Because of its lighter weight compared to steel, titanium has also replaced stainless steel in many construction materials. In Bangka Island, Indonesia, tin tailings have been identified as a potential source of titanium, making the analysis of titanium in these tailings highly significant. This study employed the froth flotation method, known for its simplicity, speed, and cost-effectiveness, to analyze titanium content from tin tailings. Sodium oleate was used as the frother and collector, while sodium chlorate acted as the depressant. The mass ratios of depressant to collector were varied at fixed collector amounts (1:10, 5:10, 10:10, and 15:10) and fixed depressant amounts (10:3, 10:6, 10:9, and 10:12). The highest titanium concentration (2.03%) was achieved with a mass ratio of 10:12, while the optimal titanium recovery (45.51%) in the concentrate occurred with equal amounts (3.75 g) of depressant and collector, or at a mass ratio of 10:10, at 15 minutes of flotation time and neutral pH. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses indicated that the tin tailings primarily contained silicate and zircon minerals, with traces of titanium in the form of rutile, ilmenite, and titanate. These findings contribute valuable insights for future titanium extraction and processing industries.

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1. Introduction

Titanium is a highly valuable metal with extensive industrial applications due to its exceptional corrosion resistance, moderate strength, and relatively low density. In the medical field, titanium is widely used for implants in dental prosthetics, surgical devices, and bone joints. In industry, it serves as a material for pipes, heat exchangers, and instrumentation, owing to its excellent resistance to high-temperature environments. Titanium is also employed in engine components because of its lightweight and high-performance characteristics. In marine applications, titanium's resistance to harsh conditions makes it ideal for components exposed to seawater. Additionally, its aesthetic appeal, durability, and light weight have made it popular in jewelry and sporting goods. Due to its broad range of applications, the recovery of titanium has become increasingly important. As a result, this study focuses on the recovery of titanium.

Titanium is primarily found in the minerals rutile (TiO_2) and ilmenite ($FeTiO_3$) in tin tailings. Geologically, rutile and ilmenite are found in metamorphic and igneous rocks, as well as in sedimentary deposits. Igneous rocks, such as basalt, are commonly ultramafic. Sedimentary deposits, on the other hand, are formed through weathering and erosion processes. Figure 1 shows rutile and ilmenite minerals.

Dahani et al. [1] reported high-grade ilmenite (90.46%) in Bangka tin tailings using a magnetic separator. Regarding ilmenite separation, Miao et al. [2] used Fenton oxidant in a flotation method for ilmenite recovery, Xiao et al. [3] applied a combined flotation and adsorption method to separate ilmenite and titanaugite, Tian et al. [4] used carboxylated starch in a flotation process to separate ilmenite and forsterite, and Sitepu et al. [5] reported the effect of electrical current in a magnetic separator on ilmenite recovery. On the other hand, for rutile recovery, Wahyuningsih et al. [6] re-

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ported rutile recovery from Bangka tin tailings using an HCl leaching process. Ismael et al. [7] achieved a 79% rutile recovery by applying a combination of alkaline roasting and acid leaching from solid waste tailings, and Kurniawan et al. [8] reported a rutile recovery of 92.6% from tin ore using a chemical separation technique involving peroxidation and reductive leaching with HCl.

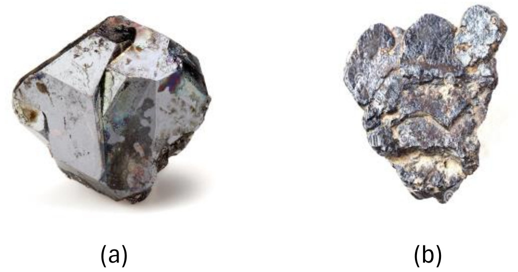

Figure 1. Rutile (a), and Ilmenite (b) minerals

In the context of titanium enrichment, Zhang et al. [9] concentrated Nb and Ti from carbonatite ore through calcining-slaking followed by gravity separation. With the rapid development of technology, the demand for titanium and titanium alloys is gradually increasing, along with the rising price of titanium materials. Therefore, titanium recovery from secondary resources, such as lithium titanate waste and residual waste, using extraction and leaching methods has gained significant interest. This is driven by the need to reduce environmental impact, utilize secondary resource waste, and sustain the titanium industry [10]. Secondary resources refer to electronic waste, including obsolete or damaged smartphones, laptops, televisions, batteries, and similar devices. Recovering valuable materials from electronic waste is an essential aspect of recycling. In contrast, primary resources refer to mined rocks or tailings that undergo exploration and exploitation to extract the desired minerals using various methods.

Although titanium recovery can be achieved using acid leaching, as reported by Dahani et al. [11], who applied sulfuric acid to recover lead from galena, this study focuses on analyzing titanium from tin tailings. After crushing and screening to obtain a specific particle size, the hydrometallurgical method of froth flotation was applied. Sodium oleate was used as both frother and collector, while sodium chlorate was employed as a depressant due to their hydrophobic and hydrophilic properties, respectively, to enhance titanium recovery and reduce impurities. Previous investigations have utilized flotation methods, such as Nie et al. [12], who reported the separation of cassiterite and calcite using cinnamon hydroxamic acid as a collector, and Tian et al. [4], who applied a starch depressant to separate forsterite and ilmenite. Feng et al. [13] used hydroxyethyl cellulose as a depressant to separate chalcopyrite and galena, while Feng et al. [14] in other experiment, employed serpentine as a depressant in the flotation separation of galena and pyrite. Recently, numerical and statistical methods have been introduced in many analytical approaches to improve the accuracy of research results. For instance, Sierra and Korotenko [15] implemented statistical analysis in the shaking table method to improve mineral recovery based on the specific gravity differences of the elements. Keshun integrated a machine learning algorithm with the shaking table method to increase mineral recovery in industrial mining [16]. Given the simplicity, speed, and low cost of the flotation method for mineral recovery, this study applied the flotation route to analyze titanium from tin tailings.

The objective of this research is to investigate the recovery and concentration of titanium from tin tailings in Bangka Island, Indonesia, using the froth flotation method. The study aims to optimize the mass ratios of sodium oleate (frother/collector) and sodium chlorate (depressant) to enhance titanium recovery and minimize impurities. By analyzing various mass ratios and flotation conditions, the research seeks to determine the optimal parameters for maximizing titanium concentration and recovery. This study provides valuable insights into the extraction and processing of titanium from secondary resources, contributing to more sustainable industrial practices.

2. Methods

2.1. Physical separation

Initially, the ore sample collected from Bangka tin tailings was crushed using a jaw crusher to reduce the particle size. The smaller particles were then ground using a hammer mill to obtain finer particles. Finally, the fine particles were sieved using a sieve shaker, yielding a powder with a particle size of 150 mesh, which was prepared for the chemical process. The particle size of 150 mesh was selected as it falls within the typical range of 80 mesh to 200 mesh, commonly applied in mineral processing to optimize surface area for subsequent treatment.

2.2. Chemical separation

This study employed a hydrometallurgical method for chemical separation, specifically the froth flotation process. The flotation process was carried out using a flotation machine (Figure 2). The sample powder, sodium oleate (frother/collector), sodium chlorate (depressant), and HCl (used as a pH regulator) were placed into the flotation cell of the machine. The pH of the solution was set to 7.0, as neutral pH was chosen due to the aqueous medium used in the process.

The addition of sodium oleate and sodium chlorate was varied to achieve different ratios, as shown in Table 1. Figure 3 illustrates the flowchart of the study.

Figure 2. Denver flotation machine

Table 1. Varied ratio of sodium chlorate depressant and sodium oleate collector at 150 mesh and pH 7.0

Sodium chlorate depressant (g)	Sodium oleate collector / frother	Ratio of sodium chlorate and sodium oleate
0.375	3.75	1:10
1.875	3.75	5:10
3.750	3.75	10:10
5.625	3.75	15:10
2.50	0.75	10:3
2.50	1.50	10:6
2.50	2.25	10:9
2.50	3.00	10:12

2.3. XRF and XRD characterization

This study used a PANalytical Minipal 4 XRF (X-Ray Fluorescence) Spectrophotometer to qualitatively and quantitatively analyze the chemical composition of the tin tailing samples with the highest titanium recovery, achieved through the flotation process. The samples were analyzed at varying concentrations of sodium oleate and sodium chlorate.

For XRD characterization, this study employed a PANalytical X'pert PRO XRD system with CuKα incident radiation (wavelength of 1.54060 Å) from a copper anode, operated at 40 kV and 30 mA. The XRD patterns of the samples were recorded in continuous mode at a scanning speed of 0.02°/min, within the 2θ range of 10° to 90°.

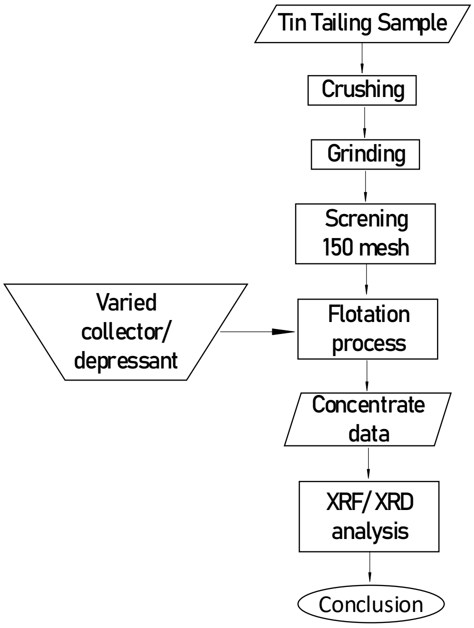

Figure 3. Flow chart of this study

3. Results and Discussion

3.1. Froth flotation

Table 2 presents the results of titanium concentration in the concentrate, corresponding to the varied ratios of sodium chlorate (depressant) and sodium oleate (frother/collector) at pH 7.0. The titanium concentration was measured using XRF analysis.

Data from Table 2 were used to create the bar chart in Figure 4, which is based on a constant mass of sodium oleate (frother/collector) and varying amounts of sodium chlorate (depressant). Figure 4 shows that increasing the amount of sodium chlorate depressant results in a decrease in titanium concentration in the concentrate. This finding is attributed to a weakened hydrophobic interaction between the sodium oleate frother and the titanium, leading to reduced titanium concentration in the concentrate. The flotation method is based on the principle of "like dissolves like." Sodium oleate, being predominantly nonpolar and hydrophobic, interacts with the desired titanium mineral, while sodium chlorate, which is primarily polar and hydrophilic, interacts with impurities. The core concept of froth flotation is that the desired mineral, in association with the frother, rises to the surface, while the polar depressant attracts impurities, which sink to the bottom of the flotation cell, enabling effective separation of the target mineral from the impurities. In a related study, Amalia [17] investigated the role of hydrophobic and hydrophilic interactions in the separation of rare earth elements using an activated carbon/palmitic acid collector.

Table 2. Results of titanium content (%) by XRF, pH 7.0, 150 mesh

Varied of ratio $NaClO_3$ and Na-oleate	Titanium concentration (%)
1:10	1.52
5:10	0.99
10:10	1.18
15:10	0.42
10:3	1.14
10:6	1.28
10:9	1.07
10:12	2.03

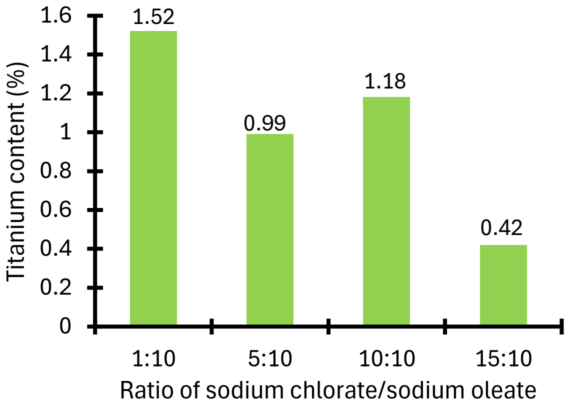

Figure 4. Titanium concentration as a function of the ratio of sodium chlorate depressant to sodium oleate collector at constant collector mass and pH 7.0

On the other hand, Figure 5 shows that increasing the amount of sodium oleate frother leads to a higher titanium concentration in the collector. This result is due to the stronger hydrophobic interaction between the sodium oleate frother and the titanium, which enhances the titanium concentration in the collector. The separation process in flotation is based on the strength of hydrophobic or hydrophilic interactions, resulting in polar-polar or nonpolar-nonpolar attractions. In this case, sodium oleate, acting as both a frother and collector, is assumed to have predominantly nonpolar characteristics, while sodium chlorate, acting as a depressant, has more polar characteristics. The interaction between titanium and the frother or depressant is influenced by the mass concentrations of these agents. In this study, sodium oleate plays a dual role as both frother and collector, whereas many other flotation processes utilize separate chemicals for these functions [12–14].

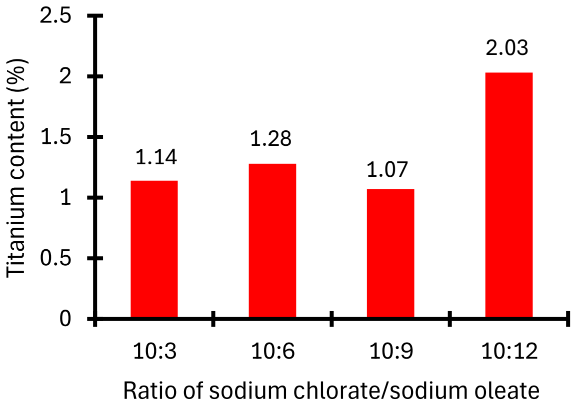

Figure 5. Titanium concentration based on ratio sodium chlorate depressant/ sodium oleate collector in constant mass depressant with pH 7.0

3.2. Titanium recovery equations

The general formula for mineral recovery is described as follows:

$$R = \frac{C.c}{F.f} \text{ x } 100\% \tag{1}$$

where C represents the concentrate mass in grams (g), c is the concentrate concentration in percentage (%), F denotes the feed mass in grams (g), and f is the feed concentration in percentage (%). The concentrate mass (C) and titanium concentration (c) at various depressant/collector ratios were obtained through material balance and from the data in Table 2. The feed mass (FFF) was kept constant at 250g, with an initial titanium concentration (f) of 0.50%.

The material balance is described by the equation:

$$F = C + D \tag{2}$$

where F represents the feed mass, C is the concentrate mass, and D denotes the depressant mass. This equation ensures that the total feed mass is equal to the sum of the concentrate and the depressant masses after the flotation process, reflecting the conservation of mass during the separation procedure.

For calculations example, a depressant/collector ratio of 10:10 (as per Table 2), the titanium recovery is calculated as:

$$\mathrm{R} = (48.22\mathrm{g} \times 1.18\%) \;/\; (250\mathrm{g} \times 0.50\%) = 45.51\%$$

And for a depressant/collector ratio of 10:12 (as per Table 2), the titanium recovery is calculated as:

$$\mathrm{R} = (27.59\mathrm{g} \times 2.03\%) \;/\; (250\mathrm{g} \times 0.50\%) = 44.80\%$$

Having used similar way as described in equations (3) and (4) for other varied ratio of sodium chlorate depressant and sodium oleate collector, it yielded data of titanium recovery (Table 3).

Regarding Table 3, the data for titanium concentration (%) were obtained from XRF measurements (Table 2), while the titanium recovery (%) was calculated using Equation (1) and (2). From the titanium recovery data (Table 3), the optimum result (45.51%) was achieved at a mass ratio of depressant to collector of 10:10. Additionally, the highest titanium recovery was obtained when equal masses of depressant and collector, specifically 3.75 g each, were used, as indicated in Table 1.

Table 3. Results of titanium recovery (%) with pH 7.0 and 150 mesh

Ratio of depressant /collector	Titanium concentration (%)	Titanium recovery (%)
1:10	1.52	27.12
5:10	0.99	39.49
10:10	1.18	45.51
15:10	0.42	39.88
10:3	1.14	43.45
10:6	1.28	30.68
10:9	1.07	32.82
10:12	2.03	44.80

It is not surprising that the equal quantities of depressant and collector at a given mass value equally attracted the titanium in the froth solution at neutral pH (pH 7.0). However, sodium oleate, with its long organic chain, exhibited a slight dominance in trapping titanium in the foam solution, likely due to its ability to reduce surface tension.

3.3. XRF results

Figure 6 presents the XRF analysis of the initial tin tailing sample, with the presence of a titanium peak clearly indicated by the red arrow in the figure.

Table 4 shows the elements found in the initial tin tailing sample, with silicon (83.80%), calcium (6.68%), and iron (5.28%) as the major elements. The high silicon content suggests that the sample is predominantly composed of quartz. The table also indicates a small amount of titanium (0.50%). Since titanium is typically found in ilmenite and rutile minerals, Dahani [1] previously reported a high-grade ilmenite content (21.36%) in Bangka tin tailings from the same region where this study's samples were collected. Zircon (2.10%) was also detected in this study, consistent with Dahani’s report of 5.85% zircon in earlier research. Additionally, trace amounts of transition elements, such as yttrium (0.48%) and rhenium (0.10%), were identified, though no rare earth elements were detected in the sample.

3.4. XRD Results

Figure 7 presents the results of the XRD analysis, identifying several minerals in the initial tin tailing sample based on their geological names. Biotite was identified as a silicate mineral, nafertisite as an iron-rich mineral, aenigmatite as a mineral containing sodium, iron, titanium, and silicon, chondrodite as a mineral containing calcium and manganese, and titanite as a titanium-bearing calcium silicate mineral.

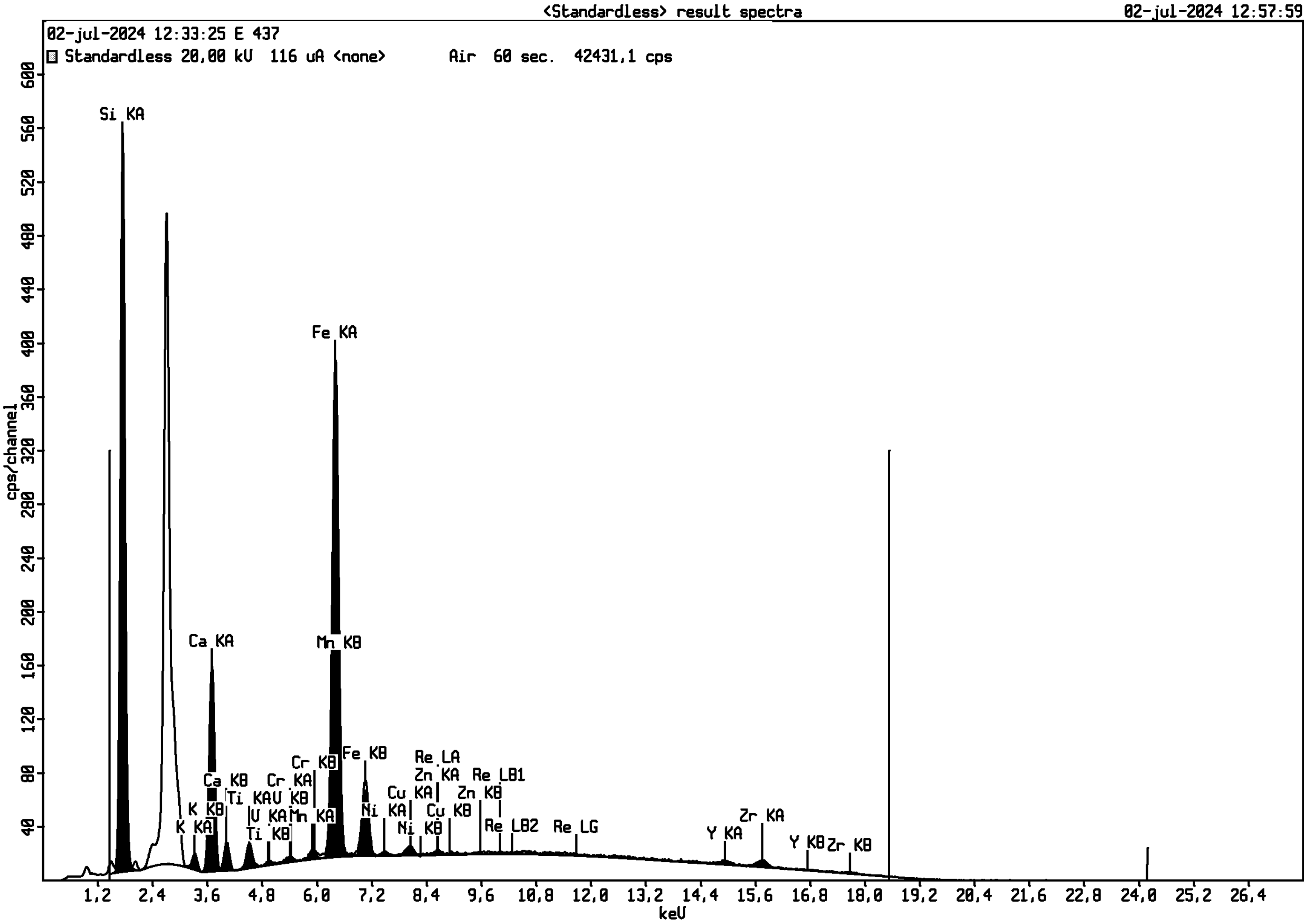

Figure 6. XRF presentation of tin tailing sample from Bangka Island

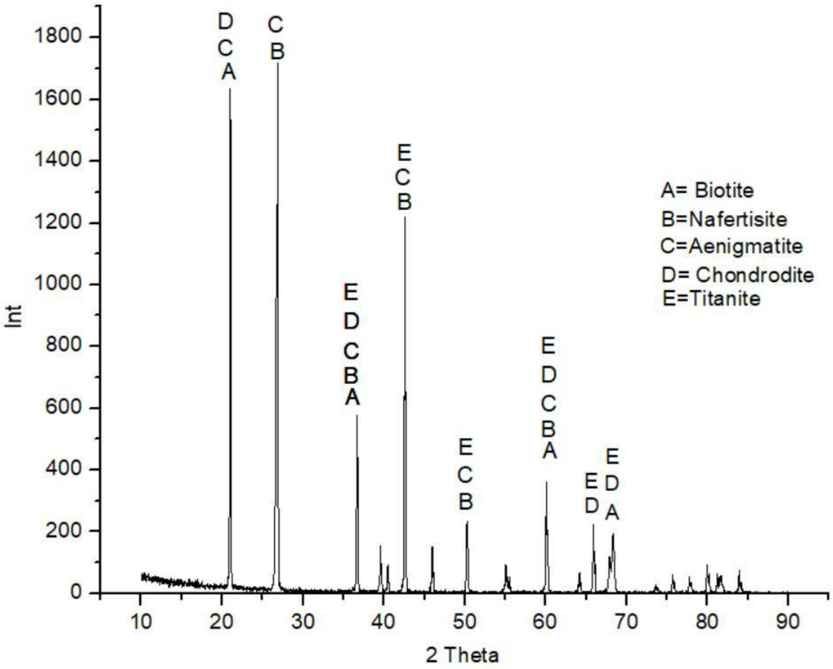

Figure 7. XRD presentation of tin tailing sample from Bangka Island

Table 4. Elements found in initial tin tailing sample using XRF analysis

Element	Concentration (%)
Silicon	83.80
Calcium	0.67
Potassium	6.68
Titanium	***0.50***
Vanadium	0.01
Chromium	0.08
Manganese	0.11
Iron	5.28
Nickel	0.04
Copper	0.10
Zinc	0.01
Yttrium	0.48
Zircon	2.10
Rhenium	0.10

The presence of these characteristic minerals is supported by the XRF analysis, as reported in Table 4. These minerals were formed in igneous and metamorphic rocks and are associated with sedimentary deposits resulting from geochemical reactions, including migration, weathering, and corrosion processes that occurred over a long period of time.

4. Conclusions

This study presents new findings on the effects of sodium chlorate (depressant) and sodium oleate (frother/collector) ratios on titanium recovery from tin tailings using the flotation method. The optimal titanium recovery (45.51%) was achieved with equal masses of depressant and frother/collector, specifically 3.75 g each, at 15 minutes of flotation time and a neutral pH of 7.0. XRF analysis revealed that the titanium-containing minerals were primarily associated with silicon and calcium, while XRD characterization identified quartz as the dominant mineral, with smaller amounts of rutile and ilmenite. Additionally, the use of low-cost chemicals provides a significant economic advantage. Future research could investigate the effects of additional variables, such as particle size, pH, and flotation time, as well as the potential benefits of using synthetic frothers or depressants to further enhance titanium recovery. In mineral processing, integrating flotation with carbon-based adsorbents, such as nanocarbon from bamboo shells or sodium palmitate derived from crude palm oil, holds promise for improving recovery in an economically viable manner.

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