



URANIUM REMOVAL FROM TIN SMELTER SLAG BY BISULFATE FUSION AND ACIDIC LEACHING

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Abstrak

Slag sebagai produk samping peleburan timah masih mengandung unsur-unsur berharga seperti Ti, Nb, Ta, Zr, Hf dan logam tanah jarang, yang memberikan prospek untuk pengolahan lebih lanjut. Perlu diperhatikan bahwa *slag* timah juga mengandung unsur-unsur radioaktif seperti Thorium (Th) dan Uranium (U), proses dekontaminasi diwajibkan untuk mengurangi kandungan kedua unsur ini, sebelum *slag* tersebut diolah. Pendekatan yang umum dilakukan untuk mengurangi kandungan U dalam *slag* seperti pelindian asam dinilai kurang efektif dikarenakan asosiasi U dengan fasa refraktori dalam slag. Untuk mendekomposisi fasa refraktori, teknik fusi sangat dipertimbangkan, sehingga dalam proses pelindian selanjutnya U dapat diperoleh menggunakan agen pelindi dengan konsentrasi asam yang rendah. Dalam penelitian ini, kalium hidrogen sulfat (KHSO₄) dan asam sulfat digunakan sebagai agen fusi dan agen pelindi. Parameter yang dipelajari yaitu rasio molar antara agen fusi dan fasa refraktori dalam slag, temperatur fusi, waktu fusi, konsentrasi asam sulfat dalam agen pelindi, dan rasio fasa cair-padat dalam tahap pelindian. Hasil penelitian menunjukkan kondisi optimum dalam perolehan U: temperatur fusi 400 °C, waktu fusi 2 jam, molar ratio 5, konsentrasi asam sulfat 2 M dan rasio fasa cair-padat 15 ml/gr. Perolehan U maksimal adalah 85,6%, sangat jauh dibandingkan dengan perolehan tanpa fusi (0,1%).

Kata Kunci: Slag timah, uranium, dekontaminasi, kalium hidrogen sulfat, fusi, pelindian

Abstract

Slag as a secondary product (waste) of tin smelter still contains not only valuable elements e.g., Ti, Nb, Ta, Zr, Hf, and rare earth elements, but also radioactive such as Th and U, which are accumulated in the slag phase during the smelting. Due to valuable element content, the slag becomes major of interest in mineral processing industries, hence the slag needs to be decontaminated before it could be processed further. The common approach to reducing U content from the slag using the leaching process is considered ineffective due to the association of U with refractory elements e.g., Si and Ti in the slag. By using a fusing agent to break down the refractory phases, the fusion approach is required in order to release U so that they could be leached out using mild lixiviant. In this research, potassium hydrogen sulfate (KHSO₄) and sulfuric acid were used as A fusing agent and lixiviant, respectively. The parameters studied include the molar ratio between fusing agent and refractory elements in slag, fusion temperature, fusion time, sulfuric acid concentration in lixiviant, and pulp density during the leaching stage. The studies so far demonstrated that optimum condition in U removal occurred at fusion temperature 400 °C, fusion time 2 hours, the molar ratio of potassium hydrogen sulfate to tin slag 5, sulfuric acid concentration 2 M and pulp density 15 ml/gr. The maximum recovery of U was 85.6%, which was significant compared to the results using direct leaching without fusion (0.1%).

Keywords: Tin slag, uranium, decontamination, potassium hydrogen sulfate, fusion, leaching

1. INTRODUCTION

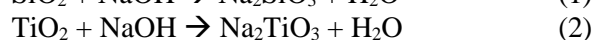
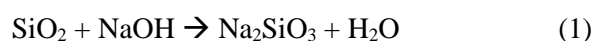
Uranium (U) is a radioactive element with a negative effect on the environment and human health, which had been extensively documented, including its deteriorating effect on the kidney, brain, lung, and heart [1]-[3]. Several activities had been known to cause the release of elements into the environment, such as mining and mineral processing [4]-[5] e.g., tin mining and processing. Tin mineral (cassiterite, SnO₂) is found together with other minerals such as monazite (Ce, La)₃PO₄, xenotime (YPO₄), and bastnasite (RE₂CO₃F), which might contain U. Preliminary separation techniques such as gravity separation, unfortunately, is incapable of separating cassiterite from U containing minerals due to almost similar density.

Cassiterite concentrate containing trace U minerals is smelted after the concentrate is mixed with flux. During smelting, the component such as silicon, titanium, and iron, including a trace of U would be bound by flux to form a separate phase i.e., tin slag (waste). The tin slag contains valuable elements such as Nb, Ta, Ti, Zr, Hf, and rare earth elements. Several studies had been conducted to recover these elements including Allain et al. [6], Brouchi and Moura [7], Gaballah et al. [8], Munir et al. [9]. Due to its attractive, economic value, thus the decontamination process is considered mandatory to minimize the release and exposure of U to the environment and humans. To the best of our knowledge, there is no publication discussing the recovery of uranium from tin slag. Hence, in this research, U recovery from tin slag would be studied using fusion followed by the leaching process.

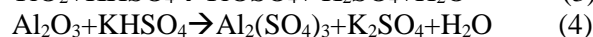
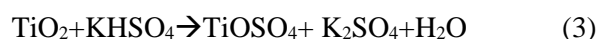
There is two metallurgical process route to recover valuable metals from slag: pyrometallurgy and hydrometallurgy. In the pyrometallurgical process, the slag is mixed with chemicals i.e., flux, collector, and reductor, which is heated to melting temperature, for example, conducted by Mudzanapabwe et al. [10] and Gustison [11]. The disadvantage of the pyrometallurgical process includes high energy consumption and only viable to handle high-grade raw materials. The second approach, hydrometallurgy, uses a chemical dissolution technique to recover the element of interest (leaching). Generally, a strong mineral acid such as nitric, hydrochloric, and sulfuric acid is employed to dissolve the elements. In the case of tin slag, Gaballah and Elain [12] had tried to use hydrofluoric acid (HF) to obtain valuable metals. The use of HF became obvious since only HF is powerful enough to dissolve silica. Other

refractory phases exist in tin slag, while another strong acid is of limited use. The use of HF is considered uneconomical due to its high price and its handling problem.

Another approach is by combining pyrometallurgy and hydrometallurgy, which is fusion followed by leaching. The fusion process, tin slag, is mixed with a fusion agent, which function is to transform the insoluble-refractory phase in the tin slag into the soluble phase in the leaching process, releasing the target elements. The process is generally done at a relatively lower temperature compared to smelting temperature. The fusion agent had been tested so far included sodium hydroxide (NaOH) by Trinopiawan et. al. [13]. In this case, refractory phases i.e., SiO₂ and TiO₂, were transformed according to equations 1 and 2.



Sodium silicate and sodium titanate produced would be easily leached using an alkaline solution. In the study, the acidic solution as a leaching agent was recommended to prevent hydrolysis (precipitation) of target elements. The disadvantage of using NaOH as a fusing agent (caustic fusion) was the excessive use of acid consumption to neutralize and high fusion temperature. These disadvantages inspired the exploration of other fusion agents to reduce fusion temperature and acid consumption in the leaching stage. Potassium hydrogen sulfate (KHSO₄) is proposed in this research due to a lower melting point (200 °C); in comparison, reaction with refractory phases such as titanium oxide and aluminum oxide occurred at around 300 and 400-550 °C, respectively (equation 3 and 4). Titanyl sulfate and aluminum sulfate produced are both easily dissolved in acidic solution especially sulfuric acid in subsequent leaching to release U dispersed inside the phases. Previous research showed that bisulfate successfully removed Th from tin slag [14].



The efficacy of potassium hydrogen sulfate as a fusion agent to release U in tin slag decontamination was investigated in this research in terms of molar ratio between refractory phases and fusion agent, fusion temperature, fusion time, sulfuric acid concentration and pulp density in subsequent leaching stage.

2. MATERIALS AND METHOD

Tin slag sample was obtained from PT Timah, Tbk. Black and glassy slag were crushed and sieved to obtained particle size finer than 150 mesh (74 microns). Before being used in the experiments, the sieved tin slag was dried in an electric oven at 120 °C for 12 hours. Chemicals used, potassium hydrogen sulfate and sulfuric acid were obtained from Merck, Darmstadt, Germany, and used as received.

In fusion experiment, tin slag was mixed with fusion agent in a porcelain crucible and mixed thoroughly. The mixture was introduced into a muffle furnace with heating speed 5 °C/min from room temperature. If the heating had been reached the desired temperature, the temperature was kept constant during pre-determined fusion time. After that, the temperature was lowered to room temperature with a cooling speed 2 °C/min.

The fusion product was then leached using sulfuric acid with varying concentrations and volume for 12 hours. The leaching residue was separated from the supernatant phase using centrifugation and decantation. The residue was then washed with Milli Q water and dried. The Th and U content in the residue was analyzed using high-resolution XRF (x-ray fluorescence) Panalytical X'Pert 3 Powder with Omnia Standard. The recovery (R) of U (decontamination) was calculated using equation 5.

$$R(\%) = \frac{(C_0 - C_E) \times 100\%}{C_n} \quad (5)$$

C₀ and C_E are metal concentrations in tin slag, before and after treatment (fusion-leaching).

3. RESULT AND DISCUSSION

3.1. Tin Slag Characterization

Tin slag characterization using XRF (x-ray fluorescence) revealed its major components, as shown in Table 1. The results showed that the major components include SiO₂ (29%), CaO (19.5%), TiO₂ (13.5%) and Al₂O₃ (11.8%), while minor components were Nb₂O₅, ZrO₂ and Fe₂O₃. Th (ThO₂) and U content in the tin slag was 0.36% and 480 ppm, respectively.

Characterization using XRD (x-ray diffraction) revealed the amorphous nature of tin slag, as shown in Figure 1. The amorphous phase is relatively easier to fuse and leach, while the results after leaching (without fusion pre-treatment) using 1 M sulfuric acid (pulp density 5 ml/gr) for 12 hours are shown in Table 1. The leaching caused the dissolution of several phases,

for example, Al₂O₃, Cr₂O₃, Fe₂O₃, and P₂O₅. Several phases became enriched, such as CaO, since CaO in the leaching process reacted with sulfuric acid to form insoluble phase CaSO₄ (anhydrite). This was confirmed by XRD (x-ray diffraction) analysis (Figure 1) on the leaching residue, which showed the peak for bassanite mineral (CaSO₄·1/2H₂O), while other relatively inert phases such as SiO₂ and TiO₂ remained amorphous. The leaching of tin slag without fusion pre-treatment did not significantly remove U (only 0.5% leached).

Table 1. Tin slag component before and after leaching treatment (without fusion). L/E is Leached (-) and Enriched (+) fraction of each phase

Phase	Before Leaching	After Leaching	Unit	L/E (%)
Al ₂ O ₃	11.84	4.51	%	61.9
CaO	19.55	22.71	%	16.2
Cr ₂ O ₃	0.54	0.32	%	-40.8
Fe ₂ O ₃	7.27	4.50	%	-38.1
K ₂ O	0.42	0.21	%	-49.5
MnO	0.71	0.47	%	-33.8
Nb ₂ O ₅	1.39	1.18	%	-14.6
Nd ₂ O ₃	0.76	0.57	%	-24.3
P ₂ O ₅	0.78	0.10	%	-87.00
SiO ₂	29.32	19.01	%	-35.2
SnO ₂	1.57	0.76	%	-51.2
ThO ₂	0.36	0.29	%	-18.7
TiO ₂	13.53	10.23	%	-24.4
U	484.80	482.40	ppm	-0.5
V ₂ O ₅	0.29	0.24	%	-18.2
Y ₂ O ₃	0.84	0.66	%	-21.7
ZrO ₂	8.50	7.74	%	-9.0

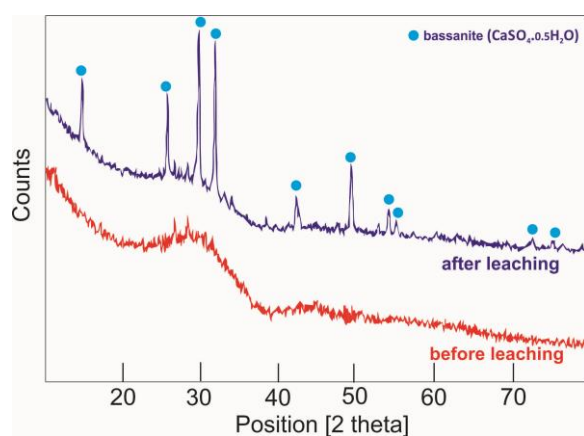


Figure 1. XRD characterization of tin slag before and after leaching without fusion pre-treatment

3.2. Effect of Fusing Agent Molar Ratio

The effect of the molar ratio of the fusing agent added to the tin slag to the U removal was studied from 1 to 6. A constant variable in this study included fusion temperature of 400 °C and fusion time 3 hours. Leaching was carried out on the fusion product for 12 hours using sulfuric acid 1 M, with pulp density 2%, which in the process, U was transferred into supernatant solution. The correlation between fusing molar ratio to the U removal is shown in Figure 2. Based on Figure 2, U removal increase to 29.7% at molar ratio 3 and increasing molar ratio did not cause a significant upgrade in its removal. Further, the molar ratio 5 would be set as optimum value and used in the subsequent experiment.

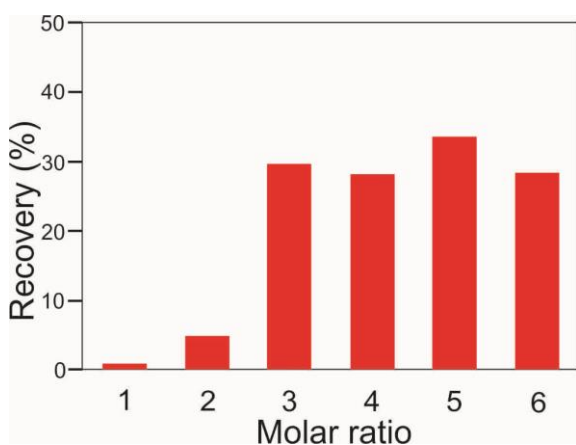


Figure 2. Effect of molar ratio of potassium hydrogen sulfate to the removal of Uranium

3.3. Effect of Fusion Temperature

The effect of fusion temperature to the tin slag decontamination was investigated at 400, 500, 600, and 700 °C, which results are shown in Figure 3. The constant variables in this temperature effect study were molar ratio 5, fusion time 3 hours, while constant leaching parameters were sulfuric acid 1 M, pulp density 0.2 kg/L, and leaching time 12 hours. Based on Figure 3, the decontamination rate decrease if the fusion temperature increased.

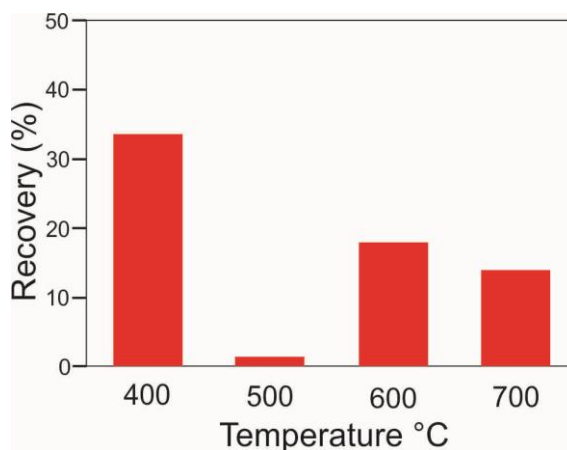


Figure 3. Effect of fusion temperature pre-treatment to the removal of Uranium

3.4. Effect of Fusion Time

The effect of fusion time was studied for 2, 3, and 4 hours duration at 400 °C. Other constant variables included molar ratio 5, leaching using sulfuric acid 1 M, pulp density 20%, and 12 hours agitation. The results are shown in Figure 4, which shows that the recovery decrease when the fusion time was extended from 2 to 3 hours, and increased back if the fusion time was prolonged to 4 hours.

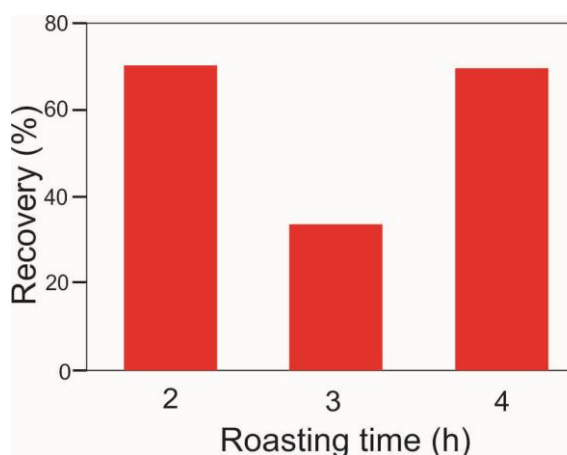


Figure 4. The effect of fusion time to the recovery of Thorium and Uranium

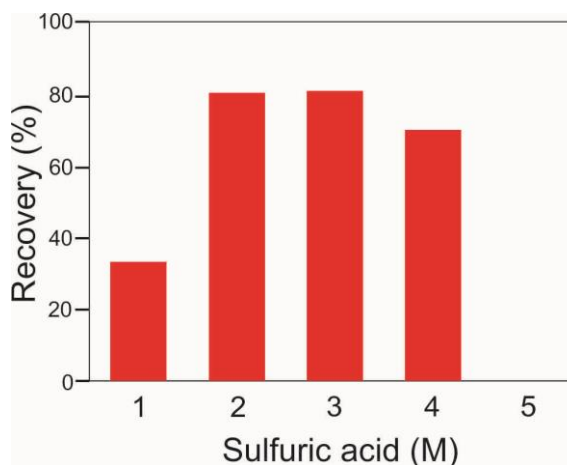


Figure 5. The effect of sulfuric acid concentration in leaching agent on Thorium and Uranium recovery

3.5. The effect of Sulfuric Acid Concentration as Leaching Agent

The effect of sulfuric acid as a leaching agent in U removal from tin slag was studied at constant variable fusion temperature 400 °C, molar ratio 5, and pulp density 0.2 kg/L and leaching time 12 hours. In contrast, sulfuric acid

concentration was varied between 1 and 5 M. The results are shown in Figure 5. Based on the investigation result, the optimum sulfuric acid concentration was 2 M, which gives U removal of 81.5%. A higher concentration of sulfuric acid decreased the recovery of U.

3.6. The Effect of Pulp Density in Leaching Stage

The effect of pulp density to remove U in tin slag after fusion pre-treatment was studied by varying the leaching agent volume from 5 to 20 ml, which was equilibrated with 1 gr of roasted tin slag (0.05 to 0.2 kg/L). A constant variable in this study included fusion temperature 400 °C, molar ratio 5, fusion time 3 hours. During leaching, sulfuric acid concentration and leaching time were kept constant at 2 M and 12 hours, respectively, while the results are depicted in Figure 6. The figure shows the optimum pulp density to be 15 ml/gr, which resulted in U removal of 85.6%. Higher pulp density did not increase the U removal significantly.

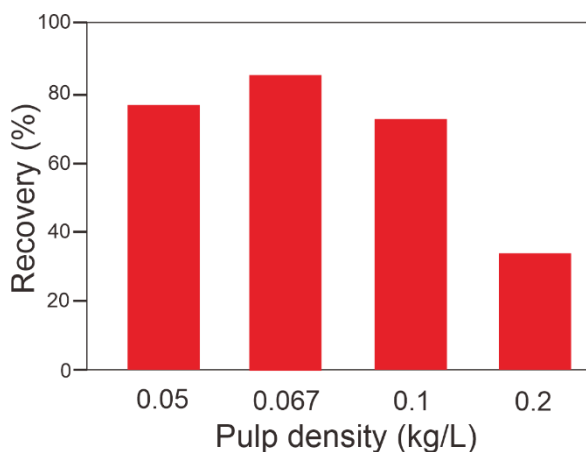


Figure 6. The effect of pulp density to the removal of Uranium

4. CONCLUSIONS

The decontamination of tin slag from Uranium (U) had been carried out using fusion pre-treatment, which was followed by leaching. Potassium hydrogen sulfate had successfully transformed the refractory phase into the soluble phase, which in the leaching stage release both U. However, the higher fusion temperature and the higher concentration of sulfuric acid as leaching agent seemed not beneficial for U removal due to the formation of calcium sulfate during leaching. The optimum condition for removal U was fusion temperature 400 °C, fusion time 2 hours, the molar ratio of potassium hydrogen sulfate to tin slag 5, sulfuric acid concentration 2 M, and pulp density 15 ml/gr.

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