Enrichment of Tantalum and Niobium Contents in Bangka Tin Slag by NaOH and H$_3$PO$_4$ Leaching

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Abstract. This study explores how 0.23% tantalum and 0.47% niobium in tin slag from the Bangka-Belitung archipelago, Indonesia, are upgraded. To enrich the contents of both metals, this research involves 8M NaOH leaching followed by 0.5M, 1M, and 1.5M phosphoric acid. First, tin slag was roasted at 900°C for 2 hours. Then, the sample was NaOH-leached while H$_3$PO$_4$ was exploited to leach its residues. Next, each of the residues from the leaching processes was characterized by XRF while the filtrates characterization used AAS and ICP-OES. On the one hand, NaOH leaching has proven to decrease the contents of iron, calcium, titanium, and aluminum. On the other hand, 0.5 M H$_3$PO$_4$ leaching optimizes tantalum contents up to 0.85% while 1.0 M H$_3$PO$_4$ leaching maximizes niobium contents up to 1.45%.

Keywords: Leaching, Niobium, Tantalum, Bangka tin slag, NaOH, phosphoric acid

1. Introduction
Investigations on environmental aspects and efforts to maximize the slag potential through metallurgical processes were carried out by previous researchers [1,2]. The results of tin slag characterization in other prior researches [3,4] show that tin slag contains uranium and thorium. Another study mentions that fluoride acid dissolution in tin slag from the Bangka-Belitung archipelago, Indonesia, causes tantalum and niobium contents to increase [5]. The exploration on tin slag from Indonesia also informs that Indonesian tin slag contains 2.7% (Ta,Nb)$_2$O$_5$ [6]. The above information indicates that, first, the adverse impact of slag processing on the environment becomes a serious problem and, therefore, the involvement of strong acids in slag processing should be minimized. Secondly, tin slag has the potential as a secondary source of tantalum and niobium oxide.
Tantalum and niobium are among 14 critical materials [7]. Having been calculated, the availability of tantalum only remains until 2020 and, more worryingly, the scarcity level of this element reaches mid term [8]. Supply and demand for these metals are unbalanced as the forecast of Ta2Os in 2015 shows that the demand for this metal exceeds 79,000 lbs and in 2016, exceeds 212,000 lbs of total supply [9].

Several previous studies were conducted to upgrade tantalum and niobium contents in tin slag [6,10–13]. Meanwhile, US Patent 3,129,896 did the separation of heavy metal constituents of tin slag, including tantalum and niobium, through electrostatic separation and roasting at 600°F [10]. By collaborating on several techniques, previous researchers extracted tantalum and columbium (niobium) carbide from tin slag through HCl and HF leaching, mixing it with carboide, and calcining it at 800°C [11]. On the other hand, HCl, HF and NaOH leaching in tin slag and acid leaching followed by alkaline and vice-versa (alkaline-acid) were able to recover tantalum from 60 to 93% and niobium from 29 to 78% and eliminate SiO2 from 40 to 78% [6]. Still involving HF, previous studies resulted in a recovery rate of 85% tin slag with (Nb+Ta)2O5 contents above 25% through the dissolution of HF or HF+H2SO4 [12]. In addition to these methods, chlorination was applied to upgrade tantalum and niobium contents in tin slag [14–16]. Other maneuvers such as caustic solution leaching, alkali pugging, alkaline fusion, and acid leaching have also proven effective to optimize the contents of Ta2Os dan Nb2O5 to 10.4% and 10.6%, respectively [13]. Among prior researches, there is an investigation applying formation of tin slag into a metal matrix composite (MMC) to effectively increase tantalum and niobium carbide contents up to 12.49% and 31.81%, respectively [17].

Not only the above studies, but some of the following explorations also focus on enriching tantalum and niobium contents. Dissolving hydrochloric acid in Bangka tin slag to upgrade tantalum and niobium contents was able to maximize the two-metals contents up to 0.664% and 1.339%, respectively [5]. Research on raising rare earth, including tantalum, contained in Bangka tin slag exploited thermodynamic software to predict chemical reactions, and Pourbaix diagrams [18].

This study aims at enriching the contents of both tantalum and niobium in Bangka tin slag through roasting at 900°C, water-quenching, and NaOH followed by H3PO4 leaching. These leachings will separate valuable oxides from the non-valuable ones so that the extraction of tantalum and niobium can be maximized.

2. Methodology

2.1. Materials and Apparatus

The sample, tin slag, was taken from a tin smelter in the Bangka-Belitung archipelago, Indonesia. The leaching solutions consist of 8M sodium hydroxide (technical) and 0.5M, 1M, and 1.5M phosphoric acid (p.a). The research equipment includes a ball mill (Toptek Topvert G1), a sieve, a Barnstead Thermolyne Furnace, a ceramic container, a magnetic stirrer (Thermo Scientific CIMAREC), and characterization equipment consisting of an X-Ray Fluorence (XRF), a Bruker handheld XRF analyzer, an Atomic Absorption Spectroscopy (AAS) PerkinElmer Analyst 400, and an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) PerkinElmer Optima 8300.
2.2. Research Scheme

BTS was roasted at 900°C, water-quenched, dewatered, and sieved with grain sizes of +100, -100+150, -150+200, -200+250, and -250 mesh. -200+250 mesh samples were leached with 8M NaOH while the residues of NaOH leaching underwent 0.5M, 1M, and 1.5M H₃PO₄ leaching. The residues from all the leachings were water-quenched to remove chemical solutions and, subsequently, dewatered. The XRF characterization in this study was performed on the residues from both NaOH leaching and H₃PO₄ leaching. Meanwhile, the filtrates were characterized by AAS and ICP-OES.

Fig. 1: Research Scheme. (A) Bangka Tin Slag. (B) Furnace. (C) Water-Quenching and Dewatering Process. (D) Sieving Machine. (E) NaOH Leaching. (F) H₃PO₄ Leaching. (○) XRF. (●) AAS. (●) ICP-OES.

3. Results and Discussions

The sample was first homogenized and reduced by grain size to make the particles smoother. Then, tin slag was characterized by X-Ray Fluorescence (XRF) to determine its chemical composition. Next, the sample was roasted, and water-quenched. Last, it was leached with NaOH followed by H₃PO₄.

High-grade oxides such as Sn, SiO₂, CaO, TiO₂, Al₂O₃, Fe₂O₃, and Zr are categorized into major other oxides (MOO) amounting to 16.15%. Elements, other than valuable oxides and MOO, with a total of 83.15% are classified into elements and minor other oxides (EMO).

3.1. XRF Characterization

As shown in Table 1, the tantalum and niobium contents obtained are 0.23% and 0.47%, respectively.

| Element | XRF Characterization Results of Bangka Tin Slag |
|---------|-------------------------------------------------|
| Ta      | 0.23                                            |
| Nb      | 0.47                                            |
| Sn      | 1.78                                            |
| SiO₂    | 6.56                                            |
| CaO     | 1.22                                            |
| TiO₂    | 2.38                                            |
| Al₂O₃   | 0.52                                            |
| Fe₂O₃   | 2.36                                            |
| Zr      | 1.33                                            |
| EMO     | 83.15                                           |

0.23% tantalum and 0.47% niobium in Bangka tin slag implies that Bangka tin slag can serve as a secondary source of tantalum and niobium oxides.

3.2. Roasting at 900°C, Water-Quenching, and Sieving

Roasting tin slag at 900°C used a furnace with 1 atm pressure for 2 hours. After being roasted, the sample was water-quenched and dewatered to remove water. Next, the sample was sieved with particle sizes of +100, -100+150, -150+200, -200+250, and -250 mesh. The products of roasting, (water-) quenching, dewatering, and sieving were termed BTS-RQDS.
After being roasted, water-quenched, and sieved, the highest percentage of each-element contents in tin slag is present at different grain sizes. As for tantalum, the highest grade, 0.29%, is in -100+150 mesh while the highest contents of niobium, 0.75%, is in -200+250 mesh. These results determines that the -100+150 mesh tantalum and -200+250 mesh niobium are the right-grain size sample for the enrichment of two metals contents.

Roasting is a process that allows the thermal decomposition reactions to the tin slag pseudo-structure. Reactions that occurred in the thermal decomposition process, accompanied by thermodynamic analysis data show that all of Gibbs energy from the oxides roasting reaction in tin slag is positive. This indicates that thermal decomposition in the roasting process at 900°C did not happen in both tantalum and niobium oxide or other oxides. However, metal oxide compounds having a pseudo-structure, after undergoing both roasting and water-quenching, caused micro cracks which resulted in stretching in tin slag particles as can be seen in Fig. 2.

![Fig. 2: SEM microstructure of tin slag in 100x magnification (a) before roasting (b) after roasting at 900°C](image)

The figure above shows that the roasted tin slag have the porosity structure that next could increased the width of wetting contact areas, thus increase the process of leaching. Roasting and water-quenching were also applied to research on saprolite ores where increased roasting temperatures lead to more cracks and porosity so that the grain size became smaller [19].

### 3.3. NaOH Leaching

In 8M NaOH leaching, the researchers used BTS-RQDS measuring -200+250 mesh where Ta+Nb contents were 0.92% and EMO contents 67.26%. This leaching was performed with a 1:10 solid-liquid ratio and, therefore, the researchers prepared 176 grams of tin slag equivalent to 90 mL, and 900 mL of 8M NaOH solution. The leaching process lasted 120 minutes at a room temperature. Table 2 shows the results of XRF characterization of the residues from 8M NaOH leaching. The table shows a decrease in Si, Ti, Al, Fe, Ta, Nb, and Zr, and an increase in Ca.

| Element | BTS-RQDS -200+250 mesh | After 8M NaOH Leaching |
|---------|------------------------|------------------------|
| Ta      | 0.17                   | 0.18                   |
| Nb      | 0.75                   | 0.76                   |
| Si      | 12.89                  | 12.79                  |
| Ca      | 4.41                   | 4.42                   |
In accordance with the above table, after 8 M NaOH leaching, tantalum contents in the tin slag residues increase to 0.18% and so do niobium’s to 0.76%. This suggests that NaOH leaching significantly dissolves other oxides and, therefore, increases the contents of tantalum and niobium. In line with these findings, previous study shows the enhanced contents of tantalum and niobium triggered by the low solubility level of both precious metals in alkaline solutions [13].

\[
\begin{align*}
\text{Ta}_2\text{O}_5 + \text{NaOH} & \rightarrow \text{NaTaO}_3 + \text{H}_2\text{O} & -45.235 \text{ kcal} \\
\text{Nb}_2\text{O}_5 + \text{NaOH} & \rightarrow \text{NaNbO}_3 + \text{H}_2\text{O} & -30.400 \text{ kcal}
\end{align*}
\]

Equation above shows the negative value of Gibbs reactions and free energy towards tantalum and niobium oxides, -45.235 kcal and -30.400 kcal. This implies that the reaction is spontaneous in triggering the formation of NaTaO$_3$ and NaNbO$_3$ compounds and, furthermore, contributes to raising tantalum and niobium contents. The formation of these two compounds were observed through tantalum and niobium Pourbaix diagrams on Fig. 2.

**Fig.3:** (a) Tantalum and (b) Niobium Pourbaix diagrams in 8M NaOH (pH=14.9).

Fig. 3 (a) shows that in 8 M NaOH (pH = 14.9) leaching at 25°C, a NaTaO$_3$ compound forms. Under the same condition, NbO$_3^-$ ion also forms, as shown on Fig. 3 (b). This phenomenon indicates the partial dissolution of niobium in 8M NaOH. Meanwhile, the results of ICP-OES analysis in Table 3 shows niobium contents, 0.206 ppm.

**Table 3:** ICP-OES characterization results of 8M NaOH leaching residues.

| Element   | Content | ppm | %        |
|-----------|---------|-----|----------|
| Tantalum  | nd*     | nd* | nd*      |
| Niobium   | 0.206   | 0.00002 |

*not detected

Of the 0.206 ppm of niobium, the researchers concluded that the 8M NaOH leaching of Bangka tin slag could dissolve some niobium oxide contents.
3.4. H$_3$PO$_4$ Leaching

After being NaOH-leached, the residues were again leached with H$_3$PO$_4$. The residues from NaOH leaching were divided into three parts, each of which were 40 grams (equivalent to 25 mL). Then, to obtain a 1:10 solid-liquid ratio, the sample was dissolved with 250 mL H$_3$PO$_4$ with concentration variations of 0.5 M, 1.0 M, and 1.5 M for 2 hours. The XRF characterization results of H$_3$PO$_4$ leaching residues are provided in Table 4.

| Element | BTS-RQDS-200+250 | NaOH 8M | H$_3$PO$_4$ 0.5 M | H$_3$PO$_4$ 1.0 M | H$_3$PO$_4$ 1.5 M |
|---------|------------------|---------|------------------|------------------|------------------|
| Ta      | 0.17             | 0.18    | 0.68             | 0.79             | 0.85             |
| Nb      | 0.75             | 0.76    | 1.26             | 1.45             | 1.41             |
| Si      | 12.89            | 12.79   | 10.75            | 13.60            | 13.80            |
| Ca      | 4.42             | 4.42    | 2.60             | 3.02             | 2.80             |
| Ti      | 3.32             | 3.23    | 5.34             | 6.28             | 6.06             |
| Al      | 2.96             | 2.88    | 1.74             | 2.54             | 2.30             |
| Fe      | 4.17             | 3.78    | 5.42             | 6.02             | 5.57             |
| Zr      | 4.05             | 4.18    | 4.03             | 4.83             | 4.62             |

The data in Table 4 implies (1) that the increased concentration of H$_3$PO$_4$ raises tantalum and niobium contents and, at the same time, (2) the optimal solubility of some other oxides (Fe, Ca, and Al).

Fig. 4: The results of H$_3$PO$_4$ leaching with its concentration variations. (a) tantalum and niobium contents. (b) iron, calcium, and aluminium contents.

On the one hand, Fig. 4 (a) reveals a rise in tantalum and niobium contents in H$_3$PO$_4$ leaching residues. This phenomenon implies that tantalum contents rises as the concentration of H$_3$PO$_4$ is raised. 1.5 M H$_3$PO$_4$ leaching boosted tantalum contents four times compared to those undergoing 8M NaOH leaching.

On the other hand, Fig.4 (a) shows an increase in niobium contents in H$_3$PO$_4$ leaching residues. 1.0 M H$_3$PO$_4$ leaching optimizes niobium contents up to 1.45%. This rise is due to the niobium structure that relates directly to that of tantalum. In conclusion, if there is an increase in the contents of tantalum, there is a rise in those of niobium.

Furthermore, the researchers present the results of Gibss reactions and free energy in H$_3$PO$_4$ leaching in the equation below. Detailed description and discussion is provided in the following paragraph.
\[3\text{NaTaO}_3 + \text{H}_3\text{PO}_4 \rightarrow 1.5\text{Ta}_2\text{O}_5 + \text{Na}_3\text{PO}_4 + 1.5\text{H}_2\text{O}\]
\[\text{3NaNbO}_3 + \text{H}_3\text{PO}_4 \rightarrow 1.5\text{Nb}_2\text{O}_5 + \text{Na}_3\text{PO}_4 + 1.5\text{H}_2\text{O}\]

In equation above, tantalum has a positive \(\Delta G\) of 10.0598 kcal. This causes no spontaneous reaction during \(\text{H}_3\text{PO}_4\) leaching even though the Pourbaix diagram (Fig. 5 (a)) shows the reformation of \(\text{Ta}_2\text{O}_5\). The substance in this case is that the increase in tantalum contents occurs because the contents of the impurities are reduced. As a result, much tantalum and niobium can be extracted since no tantalum and niobium are still attached to the impurities at all. Meanwhile, Fig. 5 presents the results of Pourbaix diagram analysis of tantalum and niobium in \(\text{H}_3\text{PO}_4\) solution.

In addition, compared to the percentage of raised tantalum contents, that of increased niobium contents is lower. This is due to the dissolution of some niobium in the filtrates. This phenomenon can be seen in Table 8 above where the thermodynamic reaction of niobium with \(\text{H}_3\text{PO}_4\) produces Gibbs-negative energy, -12.192 kcal.

![Fig. 5: (a) Tantalum and (b) niobium Pourbaix diagrams in \(\text{H}_3\text{PO}_4\) solution.](image)

Fig. 5 (b) shows an analysis using the thermodynamic principle of Pourbaix diagram system \(\text{Nb}-\text{Na}-\text{O}-\text{P}-\text{H}_2\text{O}\) at 25°C. There, precisely at concentrations of 0.5 to 1.5 M \(\text{H}_3\text{PO}_4\) (pH 0.97 to 1.21), happens the dissociation of niobium which later becomes \(\text{Nb}^{3+}\) ions. This indicates that the dissociation of Nb to \(\text{Nb}^{3+}\) occurs at pH 0.97 to 1.21 and -1.25 V to 0.35 V.

Table 5 shows that niobium contents dissolved in \(\text{H}_3\text{PO}_4\) reaches an optimal value of 0.0008% at 1.5 M. The increase in tantalum and niobium contents is also due to the impurities dissolution.

| Concentration of \(\text{H}_3\text{PO}_4\) | Tantalum Content | Niobium Content |
|--------------------------------------|-----------------|-----------------|
| 0.5 M                                | nd*             | nd*             |
| 1.0 M                                | 0.400           | 0.247           |
| 1.5 M                                | 0.937           | 8.413           |
|                                      | 0.00004         | 0.00002         |
|                                      | 0.0003          | 0.0008          |

*not detected
Table above indicates the dissolved tantalum contents rise as the concentration of H₃PO₄ is raised. This is due to the rise in phosphate ions in the leaching solution. Increasing the concentration of the leaching solution also leads to more impurities dissolution. Because of the large amount of dissolved impurities, much tantalum in residues are successfully pulled or extracted from them. Through H₃PO₄ leaching, the optimal tantalum contents reach 0.85% at concentration 1.5 M. In addition, ICP-OES in Table 9 also indicates the dissolution of tantalum in H₃PO₄ solution.

The dissolution of H₃PO₄ in tin slag makes the contents of calcium and aluminum in the slag lessen compared to these two elements’ contents in BTS-RQDS and BTS-RQDS that was NaOH-leached (see Fig. 4 (b)). The reduced contents of calcium and aluminum ease the tantalum and niobium extraction so that the two metals contents become higher than their contents to which impurities still attach. This means that calcium and aluminum dissolution raises tantalum and niobium contents.

In line with the upgrading of tantalum and niobium contents in the above paragraph, in mineral ores containing both valuable oxides and non-valuable oxides, the reduction of the latter through comminution processes, in this study ‘leaching’, will maximize the extraction of the former with the result that these valuable oxides can be wholly taken (nothing still attaches to the impurities) [20]. In other words, the precious oxides which cannot be separated from the impurities will not be extracted, or thrown away along with the non-valuable oxides.

4. Conclusions
XRF Characterization of Bangka tin slag indicates that this slag can serve as a secondary source of tantalum and niobium oxide as this research reveals, that Bangka tin slag contains 0.23% tantalum and 0.47% niobium.

Through roasting at 900°C, water-quenching, and sieving, only tantalum measuring -100+150 mesh and niobium measuring -200+250 mesh are feasible for the enrichment sample of those two metals in Bangka tin slag and that in tantalum, niobium, and other oxides, no thermal decomposition in the roasting process with a temperature of 900°C happens.

After being NaOH-leached, other oxides contents are massively dissolved and, therefore, tantalum and niobium contents rise. In addition, the negative value of Gibss reactions and free energy towards tantalum and niobium oxides, -45.235 kcal and -30.400 kcal, are spontaneous in triggering the formation of NaTaO₃ and NaNbO₃ compounds which also play an active role in enriching tantalum and niobium contents.

In the process of H₃PO₄ leaching, the increasing concentration of H₃PO₄ leads to the rise in tantalum and niobium contents. In addition, H₃PO₄ leaching also makes optimum solubility in some other oxides (Fe, Ca, and Al). Another point from this leaching is the increase in tantalum contents due to the decrease in the impurities.

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