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To cite this article: Shiva F Vincia *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **547** 012049

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Study to Enhance Tantalum and Niobium Contents in Bangka Tin Slag by NaOH and HClO₄ Leaching

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Abstract. Indonesia is rich in tin ores. Slags from processing of tin ores naturally contain substantial amount of valuable metals, in this case niobium and tantalum. This research explores how niobium and tantalum contents in local Bangka tin slag can be enhanced using NaOH and HClO₄ leaching reagents. First, Bangka tin slag was NaOH-leached and, then, the slag underwent HClO₄ leaching. Before undergoing any processes, the contents of niobium and tantalum in Bangka tin slag were 0.47% and 0.23%, respectively. After passing two leaching processes, niobium and tantalum contents reached 1.28% and 0.79%, respectively.

Keywords : Leaching, Niobium, Tantalum, Bangka tin slag, NaOH, HClO₄

1. Introduction

Valuable metals such as iron, copper, lead, zinc, tantalum and niobium can be recovered from slags [1]. Information on tantalum supply deficits in 2015 and 2016 [2] challenges researchers to maximize the supply of tantalum from tin slag. Tin slags mainly spread across Nigeria, Australia, South Africa, Brazil, Zaire, Thailand, Malaysia and Indonesia [3-8]. Researchers found that acidic and alkaline leaching in tin slag increases tantalum and niobium contents [3,5,9-14]. HCl, HF, and NaOH leaching, and acid-basic as well as basic-acid leaching of tin slag could recover tantalum up to 60-93% and niobium up to 29-78% [4]. Tin slag with 2.7% (Ta,Nb)₂O₇ was dissolved in HF or HF plus H₂SO₄, and the processes effectively recovered both metals up to 85% [11]. HF & H₂SO₄ used to leach tantalum and niobium oxide in tin slag proved to successfully optimize the contents of Ta₂O₅ and Nb₂O₅ up to 10.4% and 10.6%, respectively [14].

The latest research successfully upgraded Nb₂O₅ and Ta₂O₅ contents up to 28.4% and 59.1% by HCl leaching followed by NaOH within a particle size of <150 μm [3]. Other investigations utilized 8% HF leaching and HCl leaching followed by NaOH to enrich tantalum and niobium contents up to 0.664% and 1.339%, respectively [8]. In addition, researchers could enhance 0.33% Ta₂O₅ and 0.64% Nb₂O₅ in Bangka tin slag through double leaching so that both metals contents reached 1.56% and 1.11%, respectively [15].

This study aims to enhance tantalum and niobium contents in Bangka Tin Slag by roasting, water-quenching, dewatering, sieving and leaching with NaOH followed by HClO₄.

2. Methodology



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2.1. Materials and Apparatus

Unprocessed Bangka Island tin slag was used and abbreviated as BTS (Bangka Tin Slag) while the slag which undergone roasting 900°C , water-quenching, dewatering, and sieving is abbreviated as BTS-RQDS. The leaching solutions contain 8M sodium hydroxide, 0.1M, 0.4M, and 0.8M perchloric acid (pa) respectively. The investigation equipment includes a ball mill (Toptek Topvert G1), a Barnstead Thermolyne Furnace, a sieve, a ceramic container, and a magnetic stirrer (Thermo Scientific CIMAREC). X-Ray Fluorescence (XRF) Bruker handheld analyzer was used for chemical composition characterization of filtrate, in addition to Atomic Absorption Spectroscopy (AAS) PerkinElmer Analyst 400 and an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Perkin-Elmer Optima 8300.

2.2. Research Procedure

After XRF characterization, BTS were roasted, water-quenched, dewatered, and +100, -100 + 150, -150 + 200, -200 + 250, and -250 mesh-sieved. Next, -200 + 250 mesh samples were leached with 8M NaOH for 2 hours at room temperature of 25°C . The volume ratio for NaOH leaching solution and the BTS-RQDS was 1:10. Based on that measure, the researchers used 90 mL tin slag (176 g) and 900 mL of 8M NaOH solution. To separate residues from filtrates in the products of NaOH leaching, a filtering paper was used. The residues were washed with aquadest to completely remove NaOH solution and dried in an oven at 100°C for 2 hours.

The residues from 8M NaOH leaching was then leached by 0.1 M, 0.4 M, and 0.8 M HClO_4 . The volume ratio between the HClO_4 leaching solution and the residues from 8M NaOH leaching was 1:10. Based on this measure, 30 mL (50 grams) residues and 300 ml HClO_4 solution were provided. The leaching process was carried out for 2 hours at room temperature of 25°C . The research procedure is given in Fig.1.

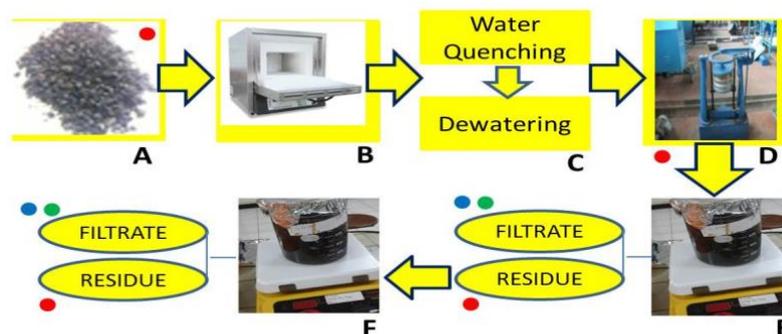


Fig. 1: Research Procedure. (A) Bangka Tin Slag. (B) Roasting in A Furnace. (C) Water-Quenching and Dewatering. (D) Sieving. (E) NaOH Leaching. (F) HClO_4 Leaching. (●) XRF Characterization. (●) AAS Characterization. (●) ICP-OES Characterization.

3. Results and Discussions

The stages of BTS processing include XRF characterization, roasting, water-quenching, dewatering, sieving, and NaOH leaching followed by HClO_4 . The elements in BTS are grouped into 3. The first group contains two valuable oxides, tantalum and niobium. The second one is called the major other oxides (MOO) which are comprised of SiO_2 , CaO , TiO_2 ,

Al₂O₃, Fe₂O₃, Sn, and Zr. Group three are elements and minor other oxides (EMOs) which encompass oxides and chemical elements not categorized into tantalum, niobium, and MOO.

3.1. XRF Characterization of BTS

The BTS characterization results are listed in Table 1, where Ta and Nb contents are 0.23% and 0.47%, respectively. Meanwhile, the total contents of MOO, including SiO₂, TiO₂, Fe₂O₃, CaO, Al₂O₃, Zr and Sn, are 16.15% and those of EMO amount to 83.15%.

Table 1. The results of XRF characterization of Bangka Tin Slag.

Element	Nb	Ta	SiO ₂	TiO ₂	Fe ₂ O ₃	CaO	Al ₂ O ₃	Zr	Sn	EMO
Content (%)	0.47	0.23	6.56	2.38	2.36	1.22	0.52	1.33	1.78	83.15

The contents of Ta and Nb, 0.23% and 0.47%, in BTS in this investigation are lower than those in the previous research, 0.33% Ta₂O₅ and 0.64% Nb₂O₅ [9,17].

3.2. Roasting, Water-Quenching, Dewatering, and Sieving of BTS

On Fig. 1, the largest tantalum and niobium contents are in the particle size of -100 + 150 mesh, the highest tin contents in that of -200 + 250 mesh, and the biggest SiO₂ contents in that of +100, -100 + 150, -200 +250, and -250 mesh. This implies that the optimal contents of certain oxides are present in certain grain sizes. The grain sizes with the highest tantalum and niobium contents would be the samples that were going to undergo further processes to increase the contents of both metals. On the other hand, previous researches show that +100 mesh BTS grains which have been roasted and water-quenched have the highest weight fraction [17] while in this exploration, the highest contents of oxides are in -100 + 150 mesh.

3.3. NaOH Leaching of BTS

The comparison of the contents of chemical composition between BTS and the residues from NaOH leaching shows a decrease in EMO contents, an increase in MOO contents, and a fall in tantalum contents.

Table 2. The results of XRF characterization of the residues from 8M NaOH leaching.

Element	Nb	Ta	SiO ₂	TiO ₂	Fe ₂ O ₃	CaO	Al ₂ O ₃	Zr	Sn	EMO
Content (%)	0.72	0.16	11.73	3.23	3.99	4.36	2.61	4.07	6.49	62.64

On Fig. 2, SiO₂ dominates almost all of the grain sizes, except -150 + 200 mesh. This phenomenon indicates that the dominance of SiO₂ dissolution has an effect on increasing tantalum and niobium oxide contents. Meanwhile, a previous research on the same topic also shows the dominance of SiO₂ in all grain sizes [8].

The reaction equations, from 1 to 8, below show the reactions of tantalum, niobium, and all MOO compounds. On the one hand, the reaction equations of (3), (4), (6), (7), and (8) that show the reactions of Si, Al, Ti, Fe and Zr present a small ΔG value. On the other hand, the reaction equation of (5) that shows the Ca reaction presents a positive ΔG value. The small ΔG value indicates that the smaller the ΔG is, the more spontaneous the reaction is while the positive ΔG value infers that the reaction is not working. However, Sn's reaction equation is not discussed because its reaction is not found in the database.



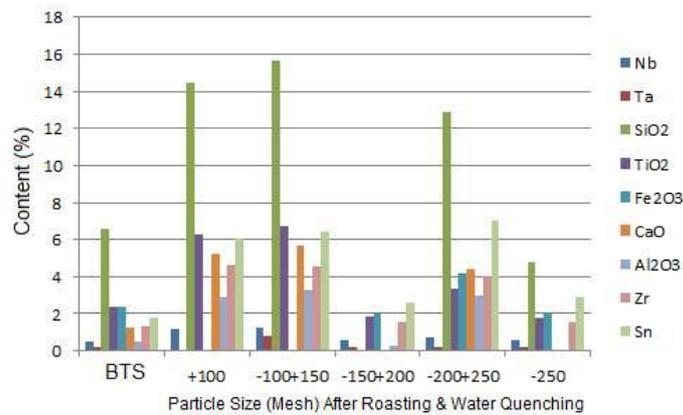


Fig. 2. The contents of oxides and other elements in BTS-RQDS according to the particle sizes. The characterization results of filtrates from NaOH leaching are listed in Table 3. The label shows the dissolution of niobium in filtrates and the not-detected tantalum.

Table 3. The results of ICP-OES characterization of filtrates from 8M NaOH leaching.

Element	Nb	Ta	Ca	Fe
Content (ppm)	0.205	not detected	not detected	2

The Eh-pH diagram maps electrochemical stability and exposes the differences of the redox reaction to an element as a pH function, whereby the presence of metal ions at certain pH and potential conditions can be revealed [16].

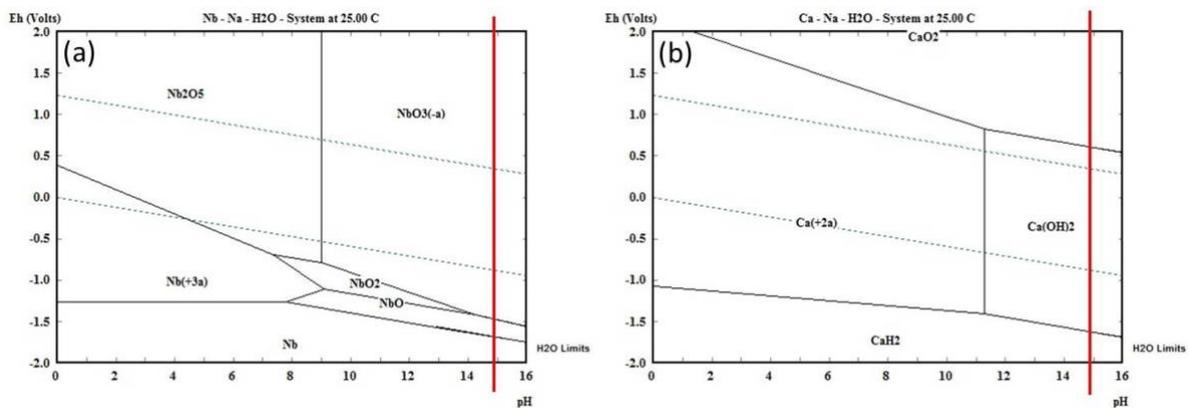


Fig. 3. Eh-pH diagrams of (a) niobium and (b) calcium.

NaOH solution is an alkaline solution, and its pH calculation is carried out by using the equation 9 below.

$$\text{pOH} = -\log [\text{OH}^-] \text{ and } \text{pH} = 14 - \text{pOH} \quad (9)$$

Previous researches show that niobium, silica, calcium, and titanium dissolve through NaOH leaching under pH condition of 10-16 [16]. Not far from the finding of the previous investigation, the pH of 8M NaOH solution in this study is 14.903. Fig. 3 (a) shows the Pourbaix diagram of Nb-Na- H₂O where at pH 14.903, the niobium element transforms into NbO³⁻ ions.

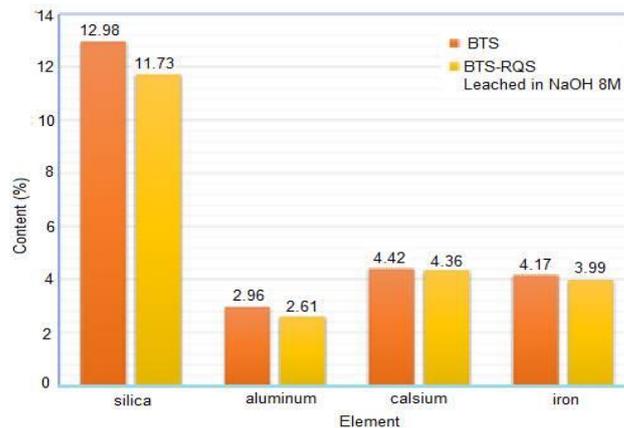


Fig. 4. The graph of silica, aluminum, calcium, and iron contents in BTS and BTS-RQS that was 8M NaOH-leached.

Fig. 4 shows the decrease in silica, aluminum, calcium, and iron contents in the residues from NaOH leaching. The reactions to NaOH and ΔG values of silica, aluminum, calcium, and iron are provided in (3), (4), (5), and (7). Based on the value of ΔG obtained, it is implied that the reaction runs spontaneously and, therefore, selective dissolution can be conducted in silica, aluminum, and iron.

The decrease in calcium contents is the lowest compared with the fall in the contents of aluminum, silica, and iron. This finding corresponds to that of C. Subramanian, et al., that it is not NaOH leaching that dissolves calcium, but acid leaching [14].

The positive ΔG value in the calcium indicates that the reactions do not work or are not spontaneous. On the other hand, pH 14.903 (Fig. 4 (b)) shows that the calcium in NaOH solution is stable in a Ca(OH)₂ compound. Table 3 presents the results of AAS characterization of filtrates from 8M NaOH leaching.

3.4. HClO₄ Leaching of BTS

The rise process in tantalum contents is from 0.70% at 0.1M HClO₄, 0.71% at 0.4M HClO₄, and 0.79% at 0.8M HClO₄. Meanwhile, niobium contents, 1.22%, at 0.1M HClO₄ rises to 1.27% at 0.4M HClO₄, and rises again to 1.28% at 0.8M HClO₄. The results of HClO₄ leaching in all concentrations (Fig. 5(a)) show that the increase in niobium and tantalum contents closely relate to that in HClO₄ concentration. Fig. 5 (b) shows that the higher HClO₄ concentration is, the more the contents of SiO₂, Fe₂O₃, and CaO decrease. The declined contents of TiO₂, Zr, and Al₂O₃ are small while Sn contents are relatively stable. This indicates that as the acid solution concentration gets bigger, the dissolution of certain

elements gets easier. The high concentration of acidic solution leads to the presence of H^+ which, then breaks the bonds between Ca, Al, Fe, and other oxides.

In the Pourbaix diagram, the different pH conditions, due to the differences of $HClO_4$ concentrations, show the difference in the form of elements, realized either in compound or ion. Therefore, this requires the calculation of $HClO_4$ acidity (pH), as shown in equation 9.

The results of filtrates, namely Nb, Ta, Ca, and Fe, characterization from $HClO_4$ leaching are provided in Table 4. In that table, calcium and iron contents become higher as $HClO_4$ concentration increases. This phenomenon indicates that the greater the concentration of $HClO_4$ is, the more Ca and Fe contents dissolve in the filtrates. This corresponds to the pH conditions of $HClO_4$ (0.096, 0.4, and 1), as shown on Fig. 6 (b) and (c) where calcium and iron contents are dominant when they transform into ions.

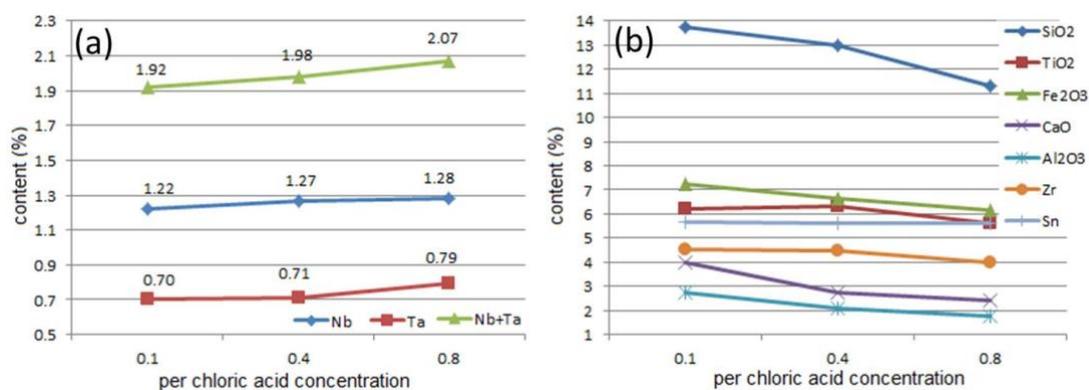


Fig. 5. The results of XRF characterization of BTS after being $HClO_4$ -leached. (a) tantalum and niobium. (b) major other oxides (MOO).

Table 4. The results of ICP-OES characterization of filtrates from $HClO_4$ leaching.

Per Chloric Acid Concentration (M)	Element (Content in ppm)			
	Nb	Ta	Ca	Fe
0.1	0,208	not detected	3,466.25	82.33
0.4	0,207	not detected	3,874.75	626.9
0.8	0,206	not detected	4,672.75	1,281.6

Fig. 6 (b) shows calcium ions in $HClO_4$ at pH 1; 0.4 and 0.096, and the stability of Ca^{2+} and $CaCl^+$ ions. This indicates that at pH 1; 0.4 and 0.096, Ca is more soluble. An earlier investigation applying the leaching of acidic solutions also shows the dissolution of Ca and other elements such as Al and Fe, except Si [5]. In addition to that, a study by Pavel Raschman, et al. shows that, various concentrations of HCl can dissolve Ca and Fe as the concentration of the solution grows higher and the longer the dissolution process then greater the solubility of calcium and iron contents is [17].

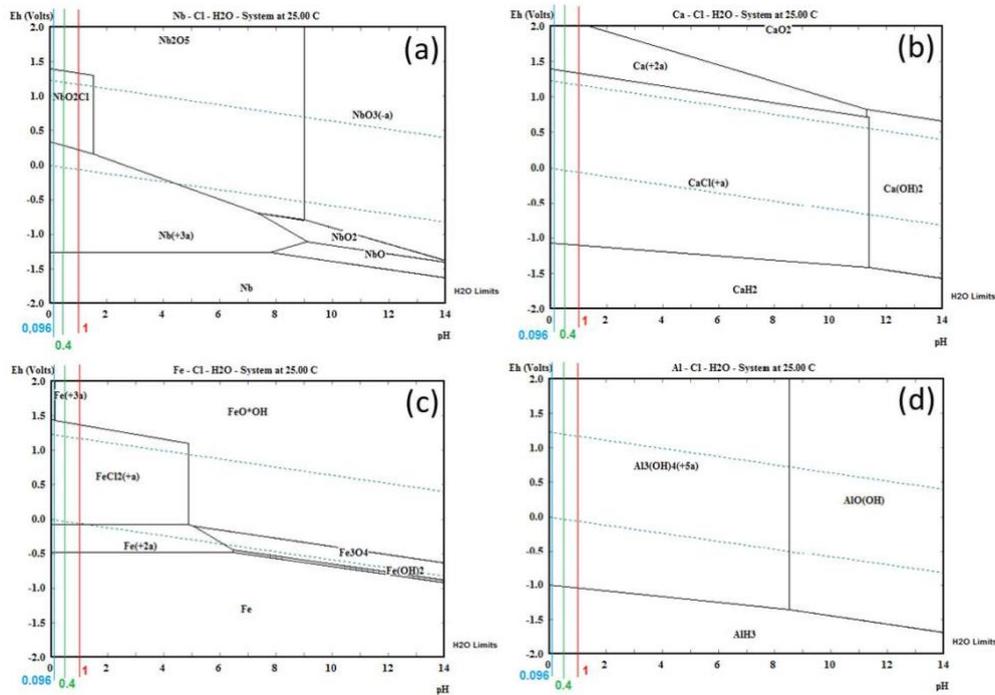


Fig. 6. Pourbaix diagrams of (a) niobium, (b) calcium, (c) iron and (d) aluminium in HClO₄ solution.

The important point of all stages of the processes above is the more the concentration of HClO₄ rises, the more the contents of Nb+Ta and EMO increase. Fig. 7 shows that the raised concentration of HClO₄ results in the increase in the contents of Nb+Ta and EMO.

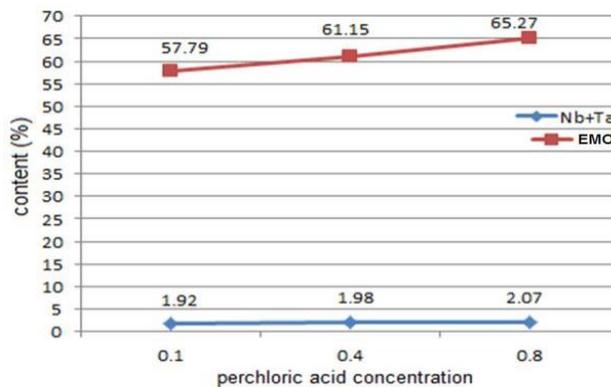


Fig.7: The contents of niobium+tantalum and EMO based on HClO₄ concentrations.

4. Conclusions

XRF characterization of pre-processing BTS shows that tantalum and niobium contents in BTS amount to 0.23% and 0.47%, respectively. After roasting, water-quenching, dewatering, and sieving of BTS, the highest contents of certain oxides are not present in all, but certain particle sizes. As the highest Ta and Nb contents are in -200 + 250 mesh, those BTS particles become the samples of the research to be further processed in order to enrich the contents of both metals.

Leaching with NaOH can dissolve of SiO₂ affects the upgrading of Ta and Nb contents and the filtrates from NaOH leaching indicate the solubility of niobium in them and on the contrary, tantalum is undetectable. After BTS is HClO₄-leached, the researchers found several results. First, the rise in the contents of Nb and Ta relates to the increase in HClO₄ concentration. Secondly, when the concentration of HClO₄ rises, the contents of Ca and Fe dissolved in the filtrates also increase. Third, pH 1; 0.4 and 0.096 causes calcium to dissolve easily. In summary, HClO₄ leaching effectively upgrades Ta, Nb, and element and minor other oxides (EMO) contents, but decreases the contents of major other oxides (MOO).

Acknowledgements

This work is financially supported by the Directorate of Research and Community Engagement, Universitas Indonesia under the 2018 PITTA program.

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