PAPER • OPEN ACCESS

Upgrading tantalum and niobium oxides content in Bangka tin slag with double leaching

To cite this article: J W Soedarsono *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **316** 012052

View the article online for updates and enhancements.

Related content

- Other Oxides Pre-removed from Bangka Tin Slag to Produce a High Grade Tantalum and Niobium Oxides Concentrate
  S Permana, J W Soedarsono, A Rustandi et al.

- New Compounds on the Base of Niobium and Tantalum Oxyfluorides
  V. T. Kalinnikov and A. I. Agulyansky

- Landscape Function of Post Tin-Mining Land After Reclamation in Bangka, Indonesia
  H F Putra, Sulistijorini and N S Aryanti

Upgrading tantalum and niobium oxides content in Bangka tin slag with double leaching

J W Soedarsono[1], S Permana[1], J K Hutauruk[1], R Adhyputra[1], A Rustandi[1], A Maksum[1,2], K S Widana[3], K Trinopiawan[3] and M Anggraini[3]

[1]Center of Minerals Processing and Corrosion Research, Department of Metallurgical and Materials Engineering,Universitas Indonesia, Depok 16424, Indonesia
[2]Department of Mechanical Engineering, Politeknik Negeri Jakarta, Depok 16425, Indonesia
[3]Nuclear Energy Agency Indonesia, Pasar Jum'at, Jakarta 12440, Indonesia

E-mail : jwsono@metal.ui.ac.id

Abstract. Tantalum has become one of the 14 types of critical materials where the level of its availability is assumed as the midterm critical metal. Benefits of the element tantalum in the electronics field increased the deficit balance of supply / demand, as more variations of electronic products developed. The tantalum experts calculated the level of availability until 2020. Base on the previous studies, tin slag is a secondary source of tantalum and niobium. This study uses tin slag from Bangka, Indonesia, abbreviated, Bangka Tin Slag (BTS). BTS was roasted, water quenched and sieved, abbreviated BTS-RQS.BTS was roasted, water quenched and sieved, abbreviated BTS-RQS.BTS-RQS was roasted at a temperature 700□C given sample code BTS-R700QS, while roasted at 800°C given sample code BTS-R800QS.A variable leaching experiment on BTS-R700QS was solvent concentration variable and on BTS-R800QS was time variable. The entire residue was characterized by X-Ray Fluorescence (XRF), and the optimum results are on the BTS-R800QS leaching into 5 M NaOH for 20 min followed by 5M HCl for 50 min, with content of Ta2O5 and Nb2O51.56% and 1.11%, respectively. The result of XRF measurement showed was the increasing of TNO content due to the increasing solvent concentration and time of acid leaching. The discussion of thermodynamics this study used was HSC Chemistry 6 as a supporting data.

Keywords: Bangka tin slag, leaching, niobium pentoxide, tantalum pentoxide, X-Ray Fluorescence.

1. Introduction
Currently, tantalum and niobium are the two of 14 critical minerals [1], counted based on tantalum midterm deposit availability until year 2020 [2]. Demand and supply in 2013 forecast of Ta_2O_5 in 2016 is minus 212,000 lbs. and in in 2015 is minus 79,000 lbs. [3]. Demand for tantalum is increasing in line with the increasing demand of high technology gadgets, as tantalum is a key element in electronics, automotive, and medicals industries [4].

Tantalite is the main mineral that contains tantalum [2], tantalite is recovered from mining and its availability in earth crust is about 2 ppm [5]. In nature, tantalum pentoxide (Ta_2O_5) is always accompanied by niobium pentoxide (Nb_2O_5). Both oxides minerals have chemical properties similarities [6]. Due to the tantalum low availability, I have done many researches to recovery

tantalum from tin slags [7–14]. Table 1 shows sources of tin slags complete with their tantalum and niobium oxides.

Previous researches have shown that Indonesian tin slags have $(TaNb)_2O_5$ at about 2.7% [8]. At recent research, Indonesian tin slags, that have $(TaNb)_2O_5$ at about 0.97%, dissolved with HF, can be increased to 2.0% of $(TaNb)_2O_5$, while dissolved with HCl followed by NaOH, can be increased to 1.71% of $(TaNb)_2O_5$[15].

Table 1. Tantalum and niobium pentoxide-containing tin slags

No.	Country	Ta_2O_5 (%)	Nb_2O_5 (%)
1.	Nigeria[7]	20.8	14.1
2.	Australia[16]	10	5.5
3.	Zaire[8]	9.8	7.8
4.	South Africa[16]	5	7
5.	Brasil[16]	1-2	2-4
6.	Thailand[17]	0.9	1.4
7.	Malasyia[18]	0.55~8.16	1.33~5.57
8.	Indonesia[15]	0.33	0.64

Methods used to increase TNO contents of tin slags in previous researches are: electromagnetic separation [19], dissolution in hydrochloric acid and hydrofluoric acid followed by decalcination at 800°C, then by final melting with carbon [9], alkaline and acid washing, then concentrates is applied by selective carbochlorination at temperature lower than 500°C [10], dissolved with $HF-H_2SO_4$[12], Chlorination (Cl_2+N_2 or Cl_2+CO+N_2) at 500-1,000°C[11], in situ carbothermic reduction using coarse concentrates powder with collie coal reductor and metallurgical cokes at 1,200-1,400°C[13], chlorination with chlorine gas in front of hydrochloric acid leaching and chlorination with carbon tetrachloride vapor at a relatively low temperature[14], separation with magnetic properties is choosen in increasing tantalume and niobium contents due to their low magnetic properties[20].

The aim of this research is to upgrading TNO contents in tin slags with different roasting temperatures, leaching concentration and time variations. This research will see the effects of roasting at 700 and 800°C, both followed by water quenching - sieving; BTS-R700QS leaching, in an alkaline followed by acid with concentrations variations in constant leaching time; also the effects of BTS-R800QS, in an alkaline followed by acid leaching with time variations, to TNO contents.

2. Experiment

2.1. Materials

Tin slag samples in this research were from PT. Timah Tbk., Indonesia. Characterization result of beginning BTS by X-Ray Fluorescent (XRF) Spectro Xepos Ametek was presented on previous research [15]. This study used two abbreviations namely MOO and EMO. MOO is short for major other oxides, MOO are SiO_2, CaO, TiO_2, Al_2O_3, Fe_2O_3 and ZrO_2. EMO stands for element and minor other oxides, EMO are oxides and elements not present in MOO, Ta_2O_5 and Nb_2O_5. This research uses leaching solutions of 1M, 4M and 5M HCl, also 1M, 4M and 5M NaOH (technical solution). The leaching equipment used was magnetic stirrer IKAMAG RH motor with adjustable motor and speed (at scale 3, displayed dial are 0-6, the speed range 100-200 rpm). This research discussion uses HSC Chemistry 6.0 software [21] as thermodynamic analysis. Fig. 1 shows this research scheme.
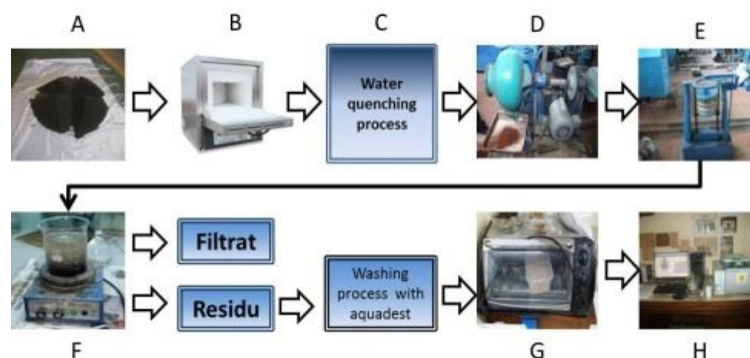
Fig. 1. Research scheme : (A) Bangka Tin Slag (B) Roasting Process (C) Water Quenching Process (D) Milling Process (E) Sieving Process (F) Leaching Process (G) Calcination Process (H) X-Ray Flouresncent analysis

2.2. Roasting Procedure

BTS was roasted at 700°C for 1 hour, water quenched and heated in oven, to vaporized its water content (BTS-R700QS). Then, sample was sieved with +100, -100+150,-150+200, -200+250 and -250 mesh and each sample was characterized with XRF.

The other BTS sample was roasted at 800°C for 1 hour, water quenched and heated in oven, to vaporize its water content (BTS-R800QS). Then, sample was sieved with +100, -100+150 and -150+200 mesh and each sample was characterized with XRF. Table 2. shows sample codes.

2.3. Leaching procedure at BTS-R700QS sample with solvent concentration variable

Sample BTS-R700QS leaching with particle size of +100 was conducted at room temperature for 30 min. The variable was leaching solution concentration.

The leaching solution used was 1 M NaOH (sample code A), while other samples with 4M NaOH (sample code D). Sample weight was 50 g and solvent volume was 500 ml. Leaching filtrate by NaOH was washed with distilled water to eliminate remaining NaOH, then, followed by calcinations in oven to remove moisture. Both calcinated samples divided into two, these four samples then used for second leaching.

Table 2. Sample codes

Sampel code	Roasting Temperature	1st Leaching	2nd Leaching
A		s : NaOH I M	
B		s : NaOH I M	s : HCl I M
C	700°c	s : NaOH I M	s : HCl 4 M
D		s : NaOH 4 M	
E		s : NaOH 4 M	s : HCl I M
F		s : NaOH 4 M	s : HCl 4 M
G		s : NaOH 5 M; t : 20 m	
H		s : NaOH 5 M; t : 20 m	s : HCl 5 M; t : 20 m
I	800°c	s : NaOH 5 M; t : 20 m	s : HCl 5 M; t : 20 m
J		s : NaOH 5 M; t : 50 m	
K		s : NaOH 5 M; t : 50 m	s : HCl 5 M; t : 50 m
L		s : NaOH 5 M; t : 50 m	s : HCl 5 M; t : 50 m

Note : s = solvent, t = time, M = Molar, m = minutes

Second leaching was applied to two samples (sample code A) with 1 M HCl and 4   M HCl (sample code B and C), and also to the other two samples (sample code D)with 1 M HCl and 4M HCl (sample code E and F). This leaching uses 400 ml solvent for each sample.

2.4. Leaching procedure at BTS-R800QS sample with time of leaching variable
BTS-R800QS sample leaching with particle size of -150+200 mesh was conducted at room temperature with leaching time variable.

First leaching was done with alkaline solution where the solid to solution ratio was 1:20. Sample BTS-R800QS of 12 g was leached with 5 M NaOH for 20 min (sample code G) and the other sample leaching were of 10 g with 5M NaOH for 50 min(sample code J). Filtrates of first leaching were washed with distilled water, then calcined in oven to remove moisture. Both calcinated samples divided into two, these four samples then used for second leaching.

Second leaching was done with solid to solution ratio of 1:30. Leaching applied to two samples G used 5 M HCl with leaching time of 20 and 50 min (samples code H and I). The other two samples J used 5M HCl with leaching time of 20 and 50 min (samples code K and L).

3. Results and discussion
On comparing the other oxide content between BTS-R700QS, particle size +100 mesh, and BTS-R800QS, particle size +150-200 mesh, SiO_2 content is decreasing while EMO content is increasing.

On previous research [15]BTS-RQS did not show content changes of SiO_2 and EMO, on the other hand, DTA-TGA characterization result showed weight decreasing starting 100°C. Table 3 shows composition of BTS, BTS-R700QS particle size +100 mesh and BTS-R800QS particle size +150-200 mesh.

Table 3. Chemical composition of BTS, BTS-R700QS (+100 mesh) and BTS-R800QS (+150-200 mesh)

Sampel	Ta_2O_5 (%)	Nb_2O_5(%)	SiO_2(%)	CaO(%)	TiO_2(%)	Al_2O_3(%)	Fe_2O_3(%)	ZrO_2(%)	EMO (%)
BTS	0.33	0.64	34.26	15.44	11.92	11.7	8.84	4.78	12.06
BTS-R700QS (+100 Mesh)	0.4	0.88	18.91	13.23	10.86	6.11	9.36	6.33	33.92
BTS-R800QS (+150-100 Mesh)	0.39	0.99	25.22	16.38	11.47	8.24	9.69	7.11	20.51

3.1. Roasting Temperature
If we look at illustration of relation between valuable mineral particles and host rock particles [22], anisothropy thermal expansion, breakage-strain and residual stress will affect liberation of valuable mineral on partially or fully locked condition. Roasting and water quenching will make valuable mineral and host rock particles bonding separation easier. Separation process is possible due to specific gravity, magnetism and solubility[23][24][25].

Roasting and quenching result on 700°C and 800°C shows that there are significant weight fraction increment of particle size -100+150, -150+200 and -200+250 mesh. At particle size +100, weight fraction is decreasing at about 50%. Previous research [15] shows the same phenomenon, so it can be concluded that decreasing particle size is effective on particle size less than 100 mesh. Fig. 2 shows relation of weight distribution to particle size of sample BTS, BTS-R700RQS and BTS-R800QS.
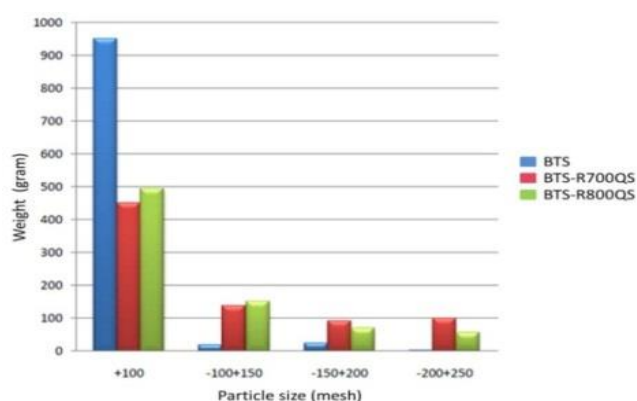

Fig.2. Weight and particle size distribution relation of BTS, BTS- R700QS and BTS-R800QS.

3.2. Leaching with concentration variation and constant time

Leaching products show maximum value, at sample code C, Ta_2O_5 and Nb_2O_5 content 1.51 and 1.03% respectively, while sample code F, Ta_2O_5 and Nb_2O_5 content 1.42 and 1.12% respectively. Alkaline leaching of sample code A shows increment of TNO content when the second leaching using higher acid concentration. Leaching at sample code D, when the first was using 1M HCl, Ta_2O_5 was decreasing to 0.614% while on the second was using acid of 4M HCl; Nb_2O_5 was decreasing to 1.12%. Fig. 3 shows the increment of TNO at sample code A after leaching with higher concentration. This can be explaining with formula (1) where solution concentration will increase reaction rate.

$$r = \frac{dC}{dt} = k. C^n \tag{1}$$

where : r = reaction rate, k= constanta, C= concentration and n = reaction order

Irregularities shown up at sample code D, after leached with increased concentration from 1M HCl to 4M HCl, Nb_2O_5 contents decreasing. Leaching conditions is more efficient at sample code A. Gibbs energy (ΔG), calculated using software[21], of sample dissolving with NaOH shows Ta_2O_5 reaction has the smallest ΔG, however it is reversible also for SiO_2, TiO_2, Al_2O_3, Fe_2O_3 and ZrO_2. Table 4 shows the reaction with NaOH followed with HCl.

Table 4. Reaction with NaOH and followed with HCl[21]

Reaction with Alkaline	Δ G (kcal)	Reaction with Acid	Δ G (kcal)
$Ta_2O_5 +2NaOH = 2\ NaTaO_3+H_2O$	-45.235	$2NaTaO_3+2HCl= Ta_2O_5+2NaCl+H_2O$	**)
$Nb_2O_5+NaOH =$*)			
$SiO_2\ +4NaOH = Na_4SiO_4+2H_2O$	**)	$Na_4SiO_4+4HCl= SiO_2+4NaCl+2H_2O$	**)
$CaO\ +NaOH=$*)			
$TiO_2\ +2NaOH= Na_2TiO_3+H_2O$	**)	$Na_2TiO3+HCl=$ *)	
$Al_2O_3+2NaOH=2NaAlO_2+H_2O$	-8.165	$NaAlO_2+4HCl=NaCl +AlCl_3+2H_2O$	**)
$Fe_2O_3+2NaOH= 2NaFeO_2+ H_2O$	-4.262	$NaFeO_2+4HCl=FeCl_3+NaCl+2H_2O$	**)
$ZrO_2+2NaOH=\ \ Na_2ZrO_3+H_2O$	-5.954	$Na_2ZrO_3+HCl=$*)	

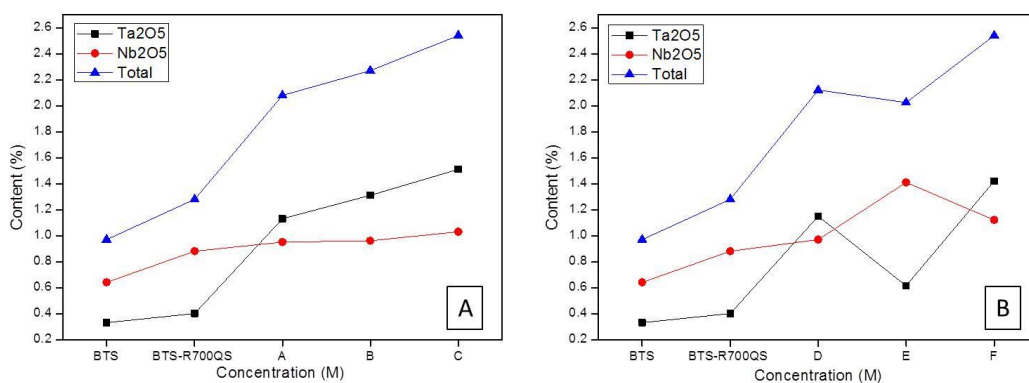*) data unavailable **) data cannot be calculated

Fig. 3. Ta_2O_5,Nb_2O5 and total content, leaching products of first leaching with
(a) 1M NaOH (b) 4M NaOH

Generally, SiO_2 and Fe_2O_3 contents are decreasing as per sample code A and D when second leaching was with1M HCl. TiO_2 content resulting increment in all leaching conditions. At leaching sample code A and D, leaching will be effective if second leaching using HCl 1 M for SiO_2 and Fe_2O_3. Fig. 4 shows SiO_2, TiO_2 and Fe_2O_3 content of leaching products with first leaching were (a) 1M NaOH (b) 4 MNaOH.
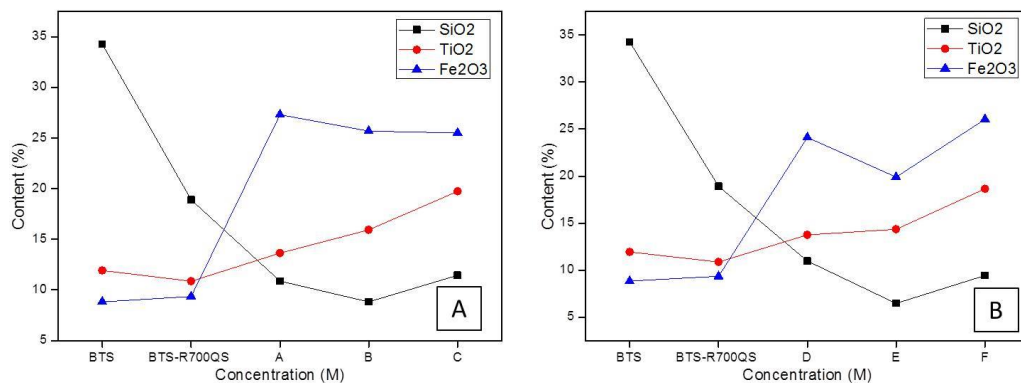
Fig. 4. SiO_2, TiO_2 and Fe_2O_3 content of leaching products with first leaching were
(a) 1M NaOH (b) 4 MNaOH

CaO and Al_2O_3 content decreasing were on sample code A and D at second leaching with 4 M HCl, while ZrO_2 decreasing was on sample code D at second leaching with4 M HCl. At leaching on sample code A and D will be effective if second leaching was with 4 M HCl for CaO and Al_2O_3 oxides. Fig. 5 shows CaO, Al_2O_3 and ZrO_2 content of leaching products with first leaching were (a) 1M NaOH (b) 4M NaOH.
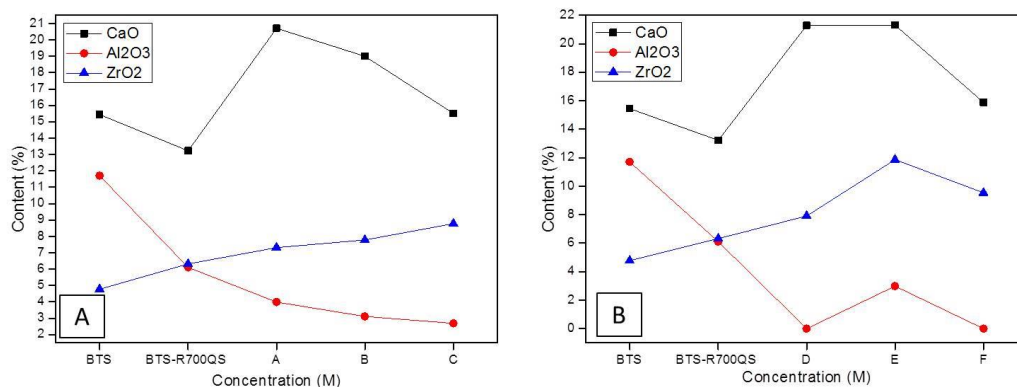
Fig. 5. CaO, Al_2O_3 and ZrO_2 content of leaching products with first leaching were
(a) 1M NaOH (b) 4M NaOH

Seeing from content increament of TNO, disolving of SiO_2, Fe_2O_3 and TiO_2, and dissolving of CaO, Al_2O_3 and ZrO_2, Dissolving with sample A and second leaching with4 M HCl gave more efficient leaching. End product of both leaching have the same TNO value, that is 2.54%.

3.3. Leaching with time and concentration variation

Leaching products reached its maximum at sample code I with Ta_2O_5 and Nb_2O_5 content are 1.56 and 1.11 % respectively. Alkaline leaching of sample code G when followed by 5M HCl leaching in 20min was resulting a decreasing Ta_2O_5 content to be 0.8%, sample code G when followed by 5M HCl leaching in 50min was resulting Nb_2O_5 content to be 1.11%. Alkaline leaching sample code J when followed with HCl 5 M leaching in 50min was resulting decreasing Nb_2O_5 content to 0.89%. Fig. 6 shows Ta_2O_5, Nb_2O_5 and total content of leaching products with 5M NaOH for time variations of (a) 20 min (b) 50 min.

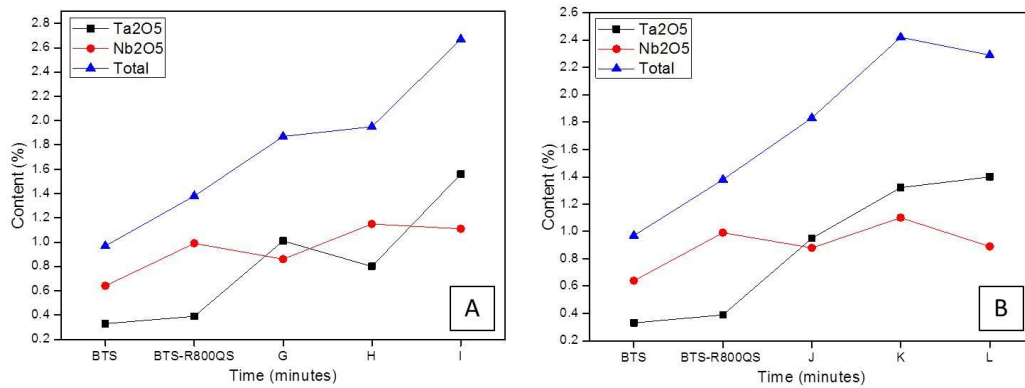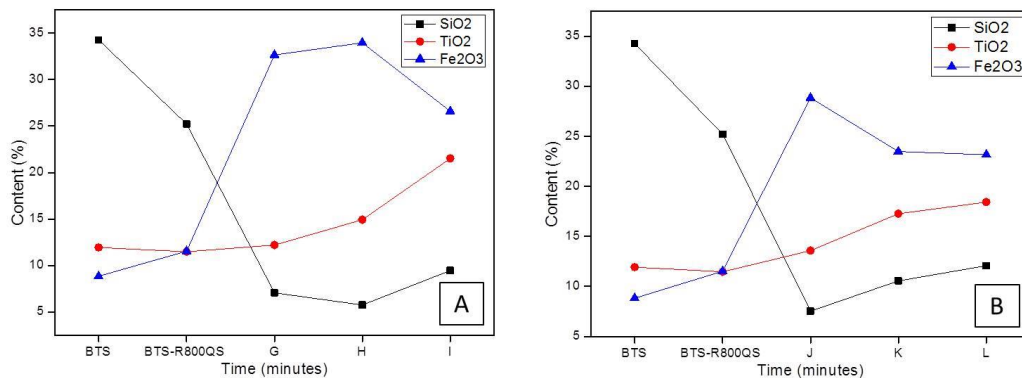Fig. 6. Ta_2O_5, Nb_2O_5 and total content of leaching products with 5M NaOH for time variations of (a) 20 min (b) 50 min.

In favorable conditions for sample code J, second leaching with 5M HCl in 50 min resulting reduction in CaO content only. For this sample code and leaching condition, all of them did not show any reduction significantly of SiO_2, TiO_2 and Fe_2O_3 oxides. Fig. 7 shows SiO_2, TiO_2 and Fe_2O_3 content of leaching products with 5M NaOH for time variations of (a) 20 min (b) 50 min.

Fig. 7. SiO_2, TiO_2 and Fe_2O_3 content of leaching products with 5M NaOH for time variations of (a) 20 min (b) 50 min.

In favorable conditions for sample code G and J, second leaching with 5M HCl in 50 min resulting reduction in CaO content only. Fig. 8 shows CaO, Al2O3and ZrO2content of leaching products with NaOH 5M for time variations of (a) 20 min (b) 50 min.
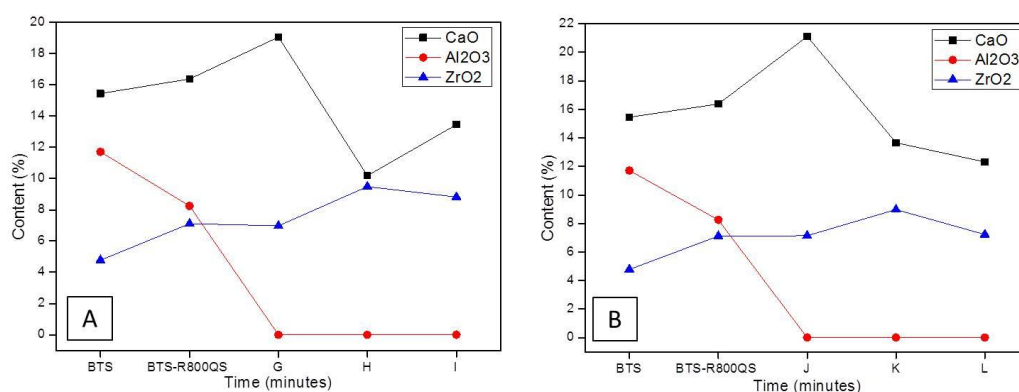
Fig. 8.CaO, Al$_2$O$_3$ and ZrO$_2$ content of leaching products with 5M NaOH for time variations of (a) 20 min (b) 50 min.

Seeing from content increament of TNO, dissolving of SiO2, Fe2O3 and TiO2, and dissolving of CaO, Al2O3and ZrO2, dissolving with sample G and second leaching with 5M HCl in 50 mingave more efficient leaching. TNO content at sample code I was 2.67%.

The final conclusion of this study, the roasting sample code BTS-R800QS with increasing leaching time (total time of 60 min for sample code C and F to of 70 min for sample code I) and increasing leaching solvent concentration producing more optimal results. However, when leaching variable increased at sample code BTS-R800QS in condition 5M NaOH in 50 min followed 5M HCl in 50 min, TNO content becomes 2.29%.

4. Consclusions
Based on the study above, upgrading TNO content in Bangka tin slag with double leaching have result as follows:
1. The particle size reduction with roasting and water quenching was effective for particle size below than 100 mesh.
2. Leaching experiments on BTS-R800QS into 5M NaOH for 20 minfollowed by 5M HCl for 50 min gave an optimum TNO grade of 2.67%.
3. Up to 5M NaOH solvent concentration concentration for 20 min followed by 5M HCl for 50 min was seen with increasing solvent concentration and leaching time of TNO content increased.
4. However, when the leaching variable was increased to a 5M NaOH solvent concentration variable for 50 min and followed by 5M HCl for 50 min, the leaching result of TNO content decreased, only 2.29%.

References
[1]   Wellmer F and Dalheimer M 2012 The feedback control cycle as regulator of past and future mineral supply Min. Depos. 47 713–29
[2]   Laura Talens Peiro, Gara Villalba Mendez R U A 2011 Rare and Critical Metals as By-products and The Implications for Future Supply
[3]   Stratton P 2013 Outlook for The Global Tantalum Market (New York)
[4]   Edmond E H and February O 2007 Commerce Resources Corporation and Tantalum
[5]   Bose D K and Gupta C K 2001 Extractive Metallurgy of Tantalum Miner. Process. Extr. Metall.

Rev. 22 389–412

[6] Ayanda O S and Adekola F A 2011 A Review of Niobium-Tantalum Separation in Hydrometallurgy J. Miner. Mater. Charact. Eng. 10 245–56

[7] Odo J.U., Okafor WC, Ekpe SO and CC. and N 2014 Extraction of Niobium from Tin Slag Int. J. Sci. Res. Publ. 4 1–7

[8] Gaballah I, Allain E, Meyer-Joly M-C and Malau K 1992 A Possible Method for the Characterization of Amorphous Slags Recovery of Refractory Metal Oxides from Tin Slags Metall. Trans. 23 249–59

[9] Cenerazzo J A, Mosheim C E, Zionsville and Corrodo E. Marvisa 1971 US Patent 3.585.024-Up Grading The Tantalum and Columbium Contents of Tin Slag 1–4

[10] Gaballah I and Allain E 1994 Recycling of Strategic Metals from Industrial Slag by a Hydro- and Pyrometallurgical Process Resour. Conserv. Recycl. 10 75–85

[11] Gaballah I, Allain E and Djona M 1997 Extraction of Tantalum and Niobium from Tin Slags by Chlorination and Carbochlorination Metall. Mater. Trans. 28

[12] Subramanian C, Suri A K and Atomic B 1998 Recovery of Niobium and Tantalum from Low Grade Tin Slag - A Hydrometallurgical Approach Environ. Waste Manag. 100–7

[13] Mudzanapabwe N T, Chinyamakobvu O S and Simbi D J 2004 In Situ Carbothermic Reduction of a Ferro-Columbite Concentrate in The Recovery of Nb and Ta as Metal Matrix Composite from Tin Smelting Slag Waste Dump Mater. Des. 25 297–302

[14] Brocchi E A and Moura F J 2008 Chlorination Methods Applied to Recover Refractory Metals from Tin Slags Miner. Eng. 21 150–6

[15] Permana S, Soedarsono J W, Rustandi A and et.al 2016 Other Oxides Pre-removed from Bangka Tin Slag to Produce a High Grade Tantalum and Niobium Oxides Concentrate IOP Conference Series : Materials Science and Engineering vol 012006 p 10

[16] Köck W and Paschen P 1989 Tantalum-processing, properties and applications Jom 41 33–9

[17] Bunnakkha C and Jarupisitthorn C 2012 Extraction of Tin from Hardhead by Oxidation and Fusion with Sodium Hydroxide 22 1–6

[18] Sulaiman M Y 1993 Simultaneous determination of thorium and uranium in tin slag Sci. Total Environ. 131 187–95

[19] Sidney M. Heins 1964 US Patent 3.129.896-Separation of Heavy Metal Contituents of Tin Slag 0–1

[20] Bulatovic S M 2010 Handbook of Flotation Reagents Vol.2 (Amsterdam: Elsevier Science & Technology Books)

[21] Roine A, Kotiranta T and et.al 2006 HSC Chemistry, Version 6.0 03 5641

[22] L. Free M 2013 Hydrometallurgy Fundamentals and Applications (United States of America: John Wiley & Sons. Inc., Hoboken, New Jersey)

[23] Callister W D and Rethwisch D G 2014 Materials Science and Engineering Materials Science and Engineering ed D Sayre (John Wiley & Sons, Inc.)

[24] Saylor D M, Rohrer G S, Carter W C, Langer S A and Jr E R F 2001 Residual-Stress Predictions in Polycrystalline Alumina J. Am. Ceram. Soc. 54

[25] Liu S, Guo Y, Qiu G and Jiang T 2013 Preparation of Ti-rich material from titanium slag by activation roasting followed by acid leaching Trans. Nonferrous Met. Soc. China 23 1174–8