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The Enhancement of Uranium and Thorium in Bangka Tin Slag

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ABSTRACT

Several studies have indicated that consumer goods, air pollution, and by-products, residues, and waste products of natural resources exploitation contain uranium and thorium. In this research, the enhancement of these two metals resulted from the extraction process of Bangka tin slag. To deal with the enhancement of uranium and thorium, Bangka tin slag (BTS) was dissolved in hydrofluoric acid (HF), hydrochloric acid (HCl), and sodium hydroxide (NaOH). The result shows that Bangka tin slag has high contents of uranium, 3404 ppm, and thorium, 25 850 ppm, which were achieved through the dissolution of BTS-roasting-quenching-sieving (BTS-RQS) residues in HF 8 %, HCl 6 M, and NaOH 10 M.

INTRODUCTION

The Regulation number 16 year 2013 on Radiation Safety in the Storage of Technologically Enhanced Naturally Occurring Radioactive Material issued by BAPETEN (Nuclear Energy Regulatory Agency of Indonesia) stipulates that the maximum permissible concentration of uranium and thorium is only 1 Bq/g, equivalent to 3 ppm uranium and 10 ppm thorium [1].

Research on historical tin and bronze artifacts from all over South Africa showed that their prime radioisotopes came from cassiterite where the tin ore evolved after crystallization through the decay of uranium (U) and thorium (Th) to lead (Pb), due to the high U/Pb ratio and other minerals [2]. A NORM site located in one of the largest rare earth deposits, Baotou, Inner Mongolia, China, has a radioactive content of 0.01-0.05 % ThO_2 and 0.0005-0.002 % U_3O_8. Converting blast furnace iron slag into cement, concrete, and bricks, or using it for road construction, has raised environmental issues.

Thus, a NORM regulatory control is very important for taking effective measures to lower its doses [3]. In Malaysia, monazite, zircon, xenotime, ilmenite, and several other minerals were obtained from tin tailings and processed further into concentrated minerals. The result of an investigation showed that the concentrated minerals contained uranium and thorium with highest concentrations of 4053 ± 428 ppm and 33 578 ± 873 ppm respectively [4]. Tin mining in Bangka Belitung Islands, Indonesia, caused the area to exhibit a higher natural radioactivity than normal areas. Research on food crops, which are the main source of exposure to internal radiation on humans, showed that the consumption of radionuclide in food was 0.205 mSv/year, far lower than the annual dose limit for the public of 1 mSv [5]. In addition to Bangka Belitung, rocks and soil in Mamuju, Sulawesi, Indonesia were known to have a high level of natural uranium and thorium radiation. It was found that the area with high thorium and uranium concentrations was related to a multi-geology process [6].

The assessment of toxic metal exposure on environment also involved biomonitoring of sewage that consisted of urine, blood, and hair [7].

To replace the imported health physics instruments, a contamination monitor was designed for detecting beta and gamma radiations emitted by radioactive materials. Indicator lamps were used to show the status of the contamination. If the value exceeded the specified levels, the monitor would provide an alarm and display the readings in the meter panel [8].

A measurement procedure with inductively-coupled plasma optical emission spectrometry (ICP-OES) can determine rare-earth metals in samples rich in tantalum and niobium. The procedure can also be applied to detect Nb, Ta, Ti, Zr, Sn, Th, and U in a single stable solution high in tantalum and niobium [9]. X-ray fluorescence (XRF) analysis was used to characterize uranium and thorium, following the standard addition quantification method. In the calibration graph, the R^2 for uranium was 0.9997 and the R^2 of thorium was 0.9915. To normalize the quantification of all other prepared samples, a visible vibration method was put to give more accurate results [10]. Tin slag samples from Butterworth were characterized with energy dispersive X-ray fluorescence (EDXRF). From those samples were obtained 60 ppm uranium and 160 ppm thorium [11]. A study on tin slag II smelting by-products found it to contain 0.0619 % of U_3O_8 and 0.53 % of ThO_2 [12]. The enrichment of BTS metal oxides indicated an increase in uranium and thorium contents [13]. Slag study increasingly flourished because of the environmental impact of both ferrous and non-ferrous slag [14].

All the measures were taken to separate radioactive and rare-earth elements in Bangka tin slag (henceforth referred to as BTS). The result showed that the two element groups could be separated through a three-stage process. The first was a 700 °C smelting with NaOH to produce silica-free hydroxide cake with 64.90 % sedimented uranium, 56.23 % thorium, and 67.67 % rare-earth metals. The second stage was leaching with H_2SO_4, and the third one was the extraction with $H_2C_2O_4$ accompanied by NH_4OH. Leaching hydroxide cake with H_2SO_4 aimed to extract radioactive elements from rare-earth elements. This produced precipitate of sodium-rare earth sulfate $NaREE(SO_4)_2$ and solution of uranium-thorium sulfate with 27.01 % dissolved uranium and 61.67 % thorium. On the other hand, rare-earth element content was only 1 %. ICP-OES analysis indicated that the reaction condition of uranium-thorium sulfate with the addition of 2.4 mmol $H_2C_2O_4$ and 32.15 mmol NH_4OH played as the optimum condition of uranium and thorium separation. In these conditions,

the precipitate contained $Th(C_2O_4)_2$ and $UO_2C_2O_4$ solution [1].

According to our latest informal discussion in 2015, the amount of BTS output of PT Timah Tbk was approximately 360 t/mo while the BTS volume at the stockyard was about 129 000 t. Based on the calculation, assuming the minimum production of tin of 35 000 t/a [15], BTS can be predicted to reach around 10 % [16], or equal to 3500 t/a of tin production. The contents of uranium and thorium in BTS enable us to have a secondary source that can be processed by reducing the contents of other oxides in it.

From the reviews above, no researchers explored how to enhance the contents of uranium and thorium in Bangka tin slag through hydrofluoric acid (HF), hydrochloric acid (HCl), and sodium hydroxide (NaOH) dissolution, and roasting-quenching-sieving (RQS).

This study investigates the enhancement of Bangka tin slag. The highest contents of the two metals can be known through the characterization of radioactive elements in (1) BTS and BTS-RQS (BTS-RQS dissolution into hydrofluoric acid), (2) BTS-RQS dissolution in hydrochloric acid, continued in sodium hydroxide, (3) BTS-RQS dissolution in acid fluoride, continued in hydrochloric acid and sodium hydroxide, and (4) chemical composition analysis using XRF and ultraviolet-visible spectrophotometry (UV-Vis).

EXPERIMENTAL METHODS

The materials used were as in previous studies [13]. Currently, BTS was characterized by SEM (scanning electron microscope) and EDS (energy dispersive X-ray spectroscopy), using FEI Inspect F50 SEM and EDAX EDS, while the samples of BTS and BTS-RQS, as well as the characterization of dissolved chemical composition, involved UV-Vis (Shimadzu UV-2101PC scanning spectrophotometer).

Previous investigations applied the procedure of pre-removed other oxides including samples F4, F8, A6B6, and A6B10 [13]. Henceforth, this study uses abbreviations MOO and EMO. MOO is a short form of major other oxides comprised of SiO_2, CaO, TiO_2, Al_2O_3, Fe_2O_3, and ZrO_2. EMO stands for elements and other minor oxides not present in MOO, uranium, and thorium.

A dissolution procedure for F4, F8, A6B6, A6B10, F4-A6B10, and F8-A6B10 was performed as in Table 1.

Table 1. Sample code, solvent type, concentration (%/M) and dissolution time (hours)

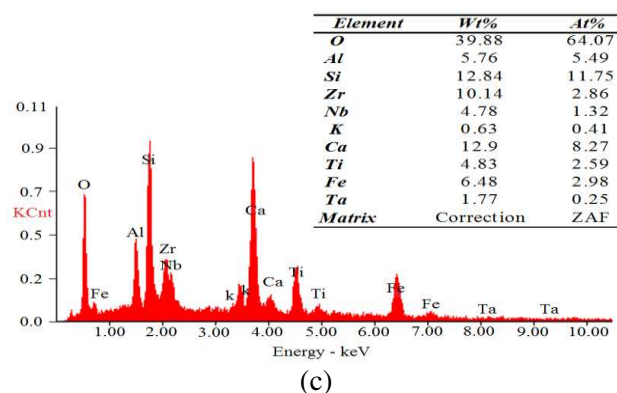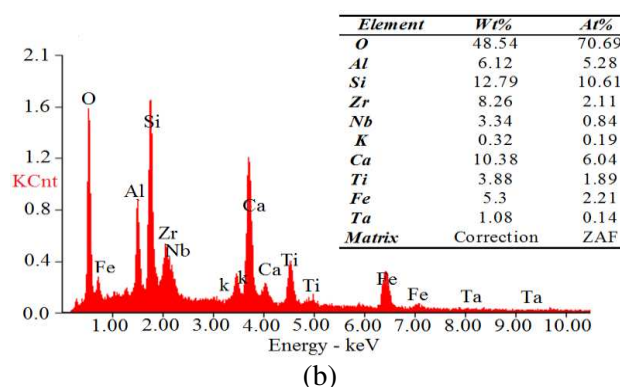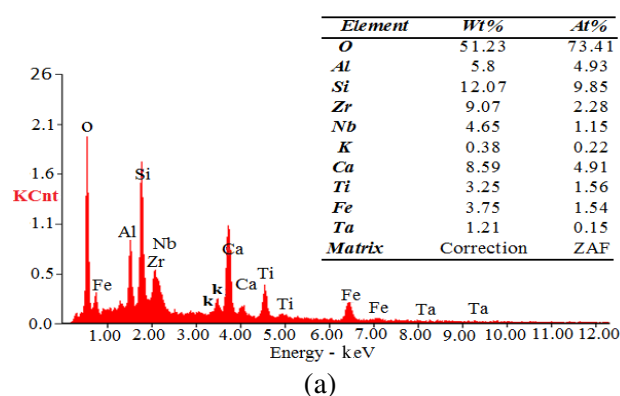| Sample Code	Type of solvent, concentration (%/M), and dissolution time (h)
F8	HF 8 % , 2 h
F16	HF 16 % , 2 h
A6B6	HCl 6 M , 2 h - next dissolution with NaOH 6 M, 20 h
A6B10	HCl 6 M , 2 h - next dissolution with NaOH 10 M, 20 h
F4-A6B10	HF 4 % , 2 h - next dissolution with HCl 6M, 2 h, last dissolution with NaOH 10 M, 20 h
F8-A6B10	HF 8 % , 2 h - next dissolution with HCl 6M, 2 h, last dissolution with NaOH 10 M, 20 h

RESULTS AND DISCUSSION

The results of the initial characterization of BTS using XRF are shown in Table 2. The table represents SiO_2, at 34.26 %, as the most prevalent content of MOO.
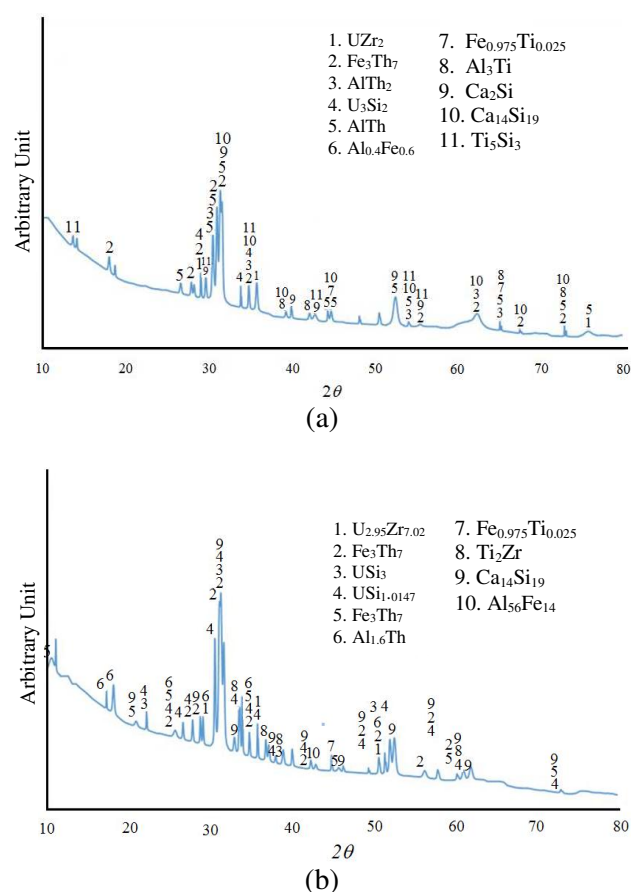
Table 2. Results of chemical analysis of the Bangka tin slag [6]

Th (ppm)	U (ppm)	SiO_2 (%)	CaO (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	ZrO_2 (%)	EMO (%)
2.028	276	34.26	15.44	11.92	11.7	8.84	4.78	12.06

Results of characterization of BTS using SEM-EDS are given in Fig. 1. The SEM-EDAX characterization shows three different values of silicon contents, 12.07 wt % in Fig. 1(a), 12.79 wt % in Fig. 1(b), and 12.84 wt % in Fig. 1(c). On the other hand, MOO was found to contain Ca, Ti, Al, Fe, and Zr.

Element	Wt%	At%
O	51.23	73.41
Al	5.8	4.93
Si	12.07	9.85
Zr	9.07	2.28
Nb	4.65	1.15
K	0.38	0.22
Ca	8.59	4.91
Ti	3.25	1.56
Fe	3.75	1.54
Ta	1.21	0.15
Matrix	Correction	ZAF

(a)

Element	Wt%	At%
O	48.54	70.69
Al	6.12	5.28
Si	12.79	10.61
Zr	8.26	2.11
Nb	3.34	0.84
K	0.32	0.19
Ca	10.38	6.04
Ti	3.88	1.89
Fe	5.3	2.21
Ta	1.08	0.14
Matrix	Correction	ZAF

(b)

Element	Wt%	At%
O	39.88	64.07
Al	5.76	5.49
Si	12.84	11.75
Zr	10.14	2.86
Nb	4.78	1.32
K	0.63	0.41
Ca	12.9	8.27
Ti	4.83	2.59
Fe	6.48	2.98
Ta	1.77	0.25
Matrix	Correction	ZAF

(c)

Fig. 1. Points of observation in sample with SEM-EDAX characterization.

Using X-ray diffraction, samples F4-A6B10 and F8-A6B10 were characterized and the results are represented in Fig. 2.

1. UZr_2
2. Fe_3Th_7
3. $AlTh_2$
4. U_3Si_2
5. AlTh
6. $Al_{0.4}Fe_{0.6}$
7. $Fe_{0.975}Ti_{0.025}$
8. Al_3Ti
9. Ca_2Si
10. $Ca_{14}Si_{19}$
11. Ti_5Si_3

(a)

1. $U_{2.95}Zr_{7.02}$
2. Fe_3Th_7
3. USi_3
4. $USi_{1.0147}$
5. Fe_3Th_7
6. $Al_{1.6}Th$
7. $Fe_{0.975}Ti_{0.025}$
8. Ti_2Zr
9. $Ca_{14}Si_{19}$
10. $Al_{56}Fe_{14}$

(b)

Fig. 2. XRD characterization results on samples with code of (a) F4-A6B10 and (b) F8-A6B10.

Sample F4-A6B10 shows an uranium compound UZr_2 at the peaks 2θ of 28.9°, 35.6°, and 75.6°. Thorium compounds appeared in Fe_3Th_7, $AlTh_2$, and AlTh. Among all, Fe_3Th_7 has dominant peaks in 2θ : 17.8°, 27.8°, 28.9°, 30.8°, 31.3°, 34.7°, 55.3°, 62.3°, 67.4°, and 72.8°. Sample F8-A6B10 reflects the uranium compounds in $U_{2.98}Zr_{7.02}$, USi_3, and $USi_{1.0147}$. $USi_{1.0147}$ is the only compound whose

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dominant peaks are in 2θ : $22°$, $25.5°$, $26.5°$, $27.7°$, $30.4°$, $31.2°$, $33.7°$, $34.6°$, $35.7°$, $37.8°$, and $42.2°$. Thorium compounds emerged from Fe_3Th_7 and $Al_{1.6}Th$. The former has dominant peaks in 2θ : $10.4°$, $20.8°$, $25.5°$, $34.6°$, $45.5°$, $49.2°$, $51.8°$, $57.7°$ $60.1°$, $60.8°$, and $72.8°$.

Samples F4-A6B10 and F8-A6B10 illustrated how easily uranium attached to zircon as in UZr_2 and $U_{2.98}Zr_{7.02}$. As for thorium, its compound often involves iron as in Fe_3Th_7.

The principle of upgrading uranium and thorium in this research is that dissolving other oxides (MOO and EMO) can increase uranium and thorium contents. The peaks in Fig. 1 (a), Fig. 1 (b), and Fig. 1 (c) are relatively similar and this illustrates the dominance of MOO.

A characterization using UV-Vis spectro-photometer resulted in (1) 72.90 mg/L thorium, in which the dilution factor was 250 times, and (2) 218.50 mg/L uranium, in which the dilution factor was 12.5. The concentration of the two minerals led their contents in BTS to be 18 225 ppm and 2731 ppm, respectively. Table 2 shows the results of BTS characterization using XRF. In this case, the thorium and uranium contents are 2028 ppm and 276 ppm, respectively.

The characterization of elements with low contents should not use XRF because the obtained results are semi-quantitative. This piece of information can be considered as a revision of the characterization of chemical composition in previous research [11,17].

Silica has a high melting point, making it difficult to dissolve in a pyrometallurgical process. Dissolving silica in hydrofluoric acid produces volatile silicon tetrafluoride, as in eq. (1).
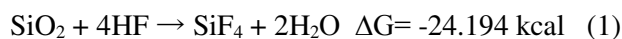
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \quad \Delta G= -24.194 \text{ kcal} \quad (1)$$

Table 3 shows the enhancement of SiO_2 through dissolution with higher concentration of hydrofluoric acid. This was described in a previous study [18]. In 16 % hydrofluoric acid, XRF analysis resulted in 1.172 % SiO_2.

**Table 3**. Results of chemical analysis of MOO and EMO in Bangka tin slag after treatment [6]

Sample code	SiO_2 (%)	CaO (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	ZrO_2 (%)	EMO (%)
F8	3.349	15.670	12.450	6.131	4.672	8.773	46.915
F16	1.172	25.530	1.236	9.301	2.843	10.600	49.064
A6B6	22.270	13.580	16.800	7.499	12.470	8.282	17.358
A6B10	22.060	12.650	18.640	6.906	12.380	8.370	17.243

Dissolution with hydrochloric acid followed by sodium hydroxide did not show a significant reduction in MOO and EMO with the same increase

of NaOH contents as that of hydrochloric acid. In this research, Ta_2O_5 and Nb_2O_5 recovery of tin slag and the contents of Ta_2O_5 and Nb_2O_5 have approximately twice the yield ratio if the particle size is smaller than 0.150 mm or the particle size between 0.180 and 0.150 mm in hydrochloric acid dissolution is followed by sodium hydroxide [19].

BTS-RQS in Fig. 3 does not show changes in the thorium contents. Thorium contents in BTS and BTS-RQS were 18 225 ppm and 18 300 ppm respectively.
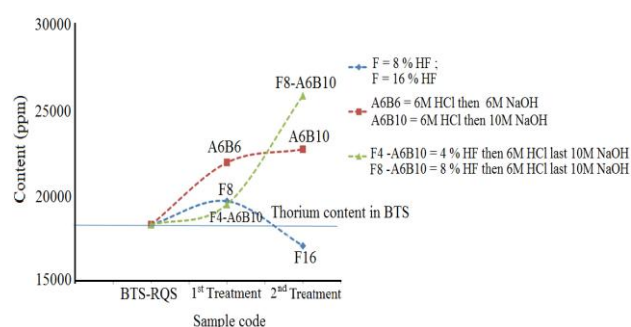
Fig. 3. Thorium content in BTS residue with various treatment conditions.

The thorium contents in sample F8, F16, A6B6, A6B10, F4-A6B10, and F8-A6B10 are shown in Fig. 3. In sample F8 and F16, the contents of thorium decreased from 19,680 ppm to 17 075 ppm while in sample A6B6 and A6B10, it increased from 21 937 ppm to 22 707 ppm. The significant enhancement occured in sample F-AB and the visible residue contents of thorium in sample F4-A6B10 is 19 490 ppm while in F8-A6B10 it is 25 850 ppm.

In Fig. 4, BTS-RQS result reflects changes in the uranium contents, from 2731 ppm in BTS to 3212 ppm in BTS-RQS.
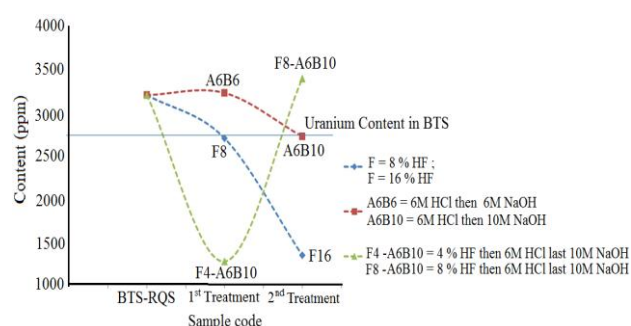
Fig. 4. Uranium content in BTS residue with various treatment conditions.

The contents of uranium in sample F8, F16, A6B6, A6B10, F4-A6B10, and F8-A6B10 are given in Fig. 3. In sample F8 and F16, the contents of uranium decreased from 2708 ppm to 1347 ppm

while in sample A6B10 and A6B6, they decreased from 3237 ppm to 2730 ppm. A significant enhancement occured in sample F-AB, in which the residues of sample F4-A6B10 was 1275 ppm and that of F8-A6B10 was 3404 ppm.

Due to a concentration increase in hydrochloric acid in sample F which resulted in a decrease in the contents of thorium and uranium, the experiments on sample F-AB used 4 % and 8 % HF.

Leaching of BTS with HCl indicated its influence on extraction of rare-earth elements. The parameters used in the investigation were acid concentration, temperature, particle size, the ratio of solid/liquid, the stirring rate of dissolution, and contact time. The result of this research is that the stirring speed parameter has no significant impacts on the extraction of rare-earth elements [20]. The common parameters that are examined both in this study and the REE extraction study referred are solvent concentration, the ratio of solid/liquid, and temperature. Table 4 presents those common parameters.

Table 4. The common research parameters of Bangka tin slag

Parametre	Radioactive elements Content	REE Extraction
Acid Concentration	HF 8%-HCl 6M-NaOH 10M	2M
S/L (gram/mL)	20	15
Temperature (^{o}C)	25	40

The next discussion is about contact time and particle size. This research was conducted with contact time of two hours for sample F, 12 hours for sample AB, and 14 hours for sample F-AB. To shorten the contact time, the temperature was raised. In the investigation of REE extraction of BTS, the optimum temperature, 40 °C, and the refinement of particle size could expand the contact surface of BTS solids and solvent.

Sample F8-A6B10 produced the optimal concentrations of thorium and uranium at 25 850 ppm and 3 404 ppm respectively.

CONCLUSION

The dissolution of BTS samples F, AB, and F-AB are summarized as follows: (i) The samples of both BTS and BTS-RQS do not show an increase in thorium contents, (ii) The contents of uranium in BTS-RQS are greater than those in BTS, (iii) Samples dissolved in hydrochloric acid shows no increases in uranium and thorium contents, whereas a decrease occurs in SiO_2 contents, (iv) The samples which were dissolved in 8 % HF, washed and dried; then dissolved into 6M HCl, washed and dried; and finally dissolved into 10 M NaOH result in the optimum contents of uranium 25 850 ppm and thorium 3404 ppm.

ACKNOWLEDGMENT

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