Initial Study for Cerium and Lanthanum Extraction from Bangka Tin Slag through NaOH and HClO₄ Leaching

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Abstract. The global demand for rare earth elements has increased dramatically for the last decade as more and more devices use rare earth elements as key for their advanced properties. The paper explores the possibility to recover cerium (Ce) and lanthanum (La) in Bangka tin slag (BTS) involving roasting at 900°C, water-quenching, and two leachings, 8M NaOH leaching and HClO₄ leaching at concentrations of 0.1M, 0.4M, and 0.8M. HClO₄ leaching causes Ce and La contents to decrease to 0.47% for 0.1M, 0.51% for 0.4M, and 0.59% for 0.8M. On the other hand, 8M NaOH optimizes cerium and lanthanum contents up to 4.35% and 1.45%, respectively.

1. Introduction

Several studies showed that metallurgical processes can be applied to extract precious metals from slag as a secondary source [1-4]. Meanwhile, other investigations expose the benefits of using non-fluoride acids to enrich valuable metals contents in slag which are environmentally friendly to the environment [5-7]. Rare Earth (RE) elements are found primarily in the ore of aluminum, copper, zinc, and nickel. The use of RE keeps increasing every year and there is little alternative or substitute materials in term of properties resulting in continuous soaring price every year. Therefore, the role of recycling is essential for RE acquisition and supply [8]. To overcome the difficulty of recycling RE from secondary sources, further exploration of processing RE cannot be ignored [9].

On the other hand, China domination in RE mining and processing as well as the decision to impose restrictions on RE export has the prices soar dramatically in 2011 [10].

In spite of all the situation concerning invaluable metals above, Indonesia may not be worried because the massive tin mining waste generated during the mining process and the post-processing slag in the Bangka-Belitung Islands has the potential to be a huge source for the supply of critical metals [2].

Tin slag is a byproduct of tin smelting. In this regard, Bangka tin slag (BTS) 1 contains 20–30% Sn while BTS 2 has a 2–3% Sn contents [11]. One tin smelter in the Bangka-Belitung archipelago, Indonesia, has a very large tin slag output [12]. Several previous studies confirmed that tin slag contains Ta and Nb [4, 13, 14, 16], U and Th [17, 18], and RE [2].

Several investigations involving the processing of critical metals are presented hereafter. The kinetics and mechanism of ammonium sulphate leaching in RE indicates the higher the leaching temperature or the smaller the particle size of the ore, the faster the leaching progress [19].

Furthermore, the solubility of RE and yttrium phosphate in aqueous solution is highly dependent on the condition of solid phase formation. Compared to the slowly formed, well-aged, and coarse precipitates, fresh sediment is much easier to dissolve. The patterns of solubility products of RE and yttrium phosphate are generally similar to the fractionation patterns which developed during phosphate coprecipitation [20].

The evaluation of chloride formation constants and fluoride–species aqua bearing from all RE III groups at temperatures up to 300°C shows that the elevated temperature of LREF²⁺ species is more stable than HREF²⁺ species (this fact is contrary to the theoretical prediction) [21].

Next, a novel approach to characterize and extract critical metals based on hydro and pyrometallurgy has been applied to tin slag. In this research, subsequent alkaline plannings and slag’s acid washing based on the pseudo-structure of amorphous materials result in (1) the selective dissolution of critical metals, (2) the low consumption of chemical reagents, mainly HF, (3) less toxic residues, and (4) high grade concentrates production, up to 60% of tantalum and niobium pentoxides with a satisfactory recovery rate about 85%. These concentrates, then, undergo selective carbon chlorination at temperatures of less than 500°C, which leads to the full extraction of niobium at 300°C and tantalum at 500°C [15].

The separation of radioactive elements and rare earth elements from BTS engages several processes. First, BTS undergoes base smelting at 700°C with
This investigation aims at recovering cerium and lanthanum contents in BTS. The recovery processes are comprised of 8M NaOH leaching followed by HClO$_4$ at concentrations of 0.1M, 0.4M, and 0.8M. From both leachings, 8M NaOH leaching has proven to be able to enhance cerium and lanthanum contents.

2. Methodology

2.1. Materials and Apparatus

The investigated tin slag was taken from a tin smelter in the Bangka-Belitung archipelago, Indonesia. Bangka tin slag is shortened to BTS. The leaching solutions include technical sodium hydroxide and perchloric acid (p.a.). The research tools consist of a Barnstead Thermolyne Furnace, a ceramic container, a ball mill (Toptek Topvert G1), a sieve, a magnetic stirrer (Thermo Scientific CIMAREC), and characterization tools: an X-Ray Flourence (XRF) Bruker handheld XRF analyzer and an Atomic Absorption Spectroscopy (AAS) PerkinElmer Analyst 400.

2.2. Research Procedure

The first step was the characterization of BTS using XRF. Next, BTS was roasted, water-quenched, and sieved. These three processes are abbreviated as RQS. After that, BTS-RQS with a size of -200 + 250 mesh was further processed with a ratio of 1:10. Based on this comparison, the researchers used 90 mL equal to 176 grams of BTS as samples and 900 mL of 8M NaOH solution. Then, the sample was leached with 8M NaOH for 2 hours at a room temperature of 25°C. After leaching, the residues and filtrates were separated by a filtering paper. The residues were then washed with aquadest to remove the residual HClO$_4$ solution. After washing, the residues were dewatered through an oven at 100°C for 2 hours. Thereafter, 8 grams of the residues from HClO$_4$ leaching were characterized by XRF while the filtrates characterization used AAS. Fig. 1 shows the details of research procedure.

![Research procedure](image)

Fig. 1. Research procedure.

3. Results and Discussion

This chapter covers several sub-chapters, including (1) BTS characterization, (2) roasting, water-quenching, and sieving of BTS, (3) NaOH leaching of BTS-RQS, and (4) HClO$_4$ leaching of the residues from NaOH leaching.

All elements and oxides in BTS are divided into 3 groups. The first group consists of two valuable oxides to be recovered, cerium (Ce) and lanthanum (La). The second one is major other oxides (MOO) that include SiO$_2$, TiO$_2$, Fe$_2$O$_3$, CaO, Al$_2$O$_3$, Zr, and Sn. The last one is comprised of elements and minor oxides (EMO) consisting of P$_2$O$_5$, Y, Bi, MnO, Nb, Ta, Th, MnO, V, Cr, W, U, Ni, Hf, Se, K$_2$O, and Ag.

3.1. BTS Characterization

The initial characterization of BTS shows cerium and lanthanum contents, 1.57% and 0.13%, respectively. The cerium contents are high compared to those in other studies, which have only 0.120% Ce$_2$O$_3$ [22]. The process of recovering Ce and La contents in this study was carried out through dissolving other oxides. Similar processes were also applied to previous dissolution studies, where red mud (wasted raw material in industrial alumina) was dissolved to recover Fe, Al, Ti, and Si [23]. Table 1 shows the details of cerium and lanthanum contents in Bangka tin slag.

| Element | Ce | La | TiO$_2$ | Zr | Sn | EMO |
|---------|----|----|---------|----|----|-----|
| Content (%) | 1.57 | 0.13 | 2.38 | 1.33 | 1.78 | 82.15 |
3.2. Roasting, Water-Quenching, and Sieving of BTS

As informed in a prior research, the roasting of tin slag causes anisotropy thermal expansion while water-quenching produces a broken strain and residual stress. Based on the grain size of tin slag, the size of the residual stress is so high that this stress creates micro cracks in tin slag [24]. Tin slag itself has an amorphous structure. This structure is always broken before deformation occurs at a room temperature. The magnitude of the fracture strength is relatively smaller than the theory of interatomic bonding. The smaller fracture strength than the interatomic bonding theory is caused by a minor defect in tin slag that can increase the stress. The rise in the stress is signified by micro cracks, internal pores, and the grain angles difficult to control [25]. Through amorphous materials, roasting, and water-quenching, oxides having weak a interatomic bonding force become easily pulled from oxides having a strong interatomic bonding force. As the processes above, cerium oxide and lanthanum in this exploration were extracted from MOO and EMO.

900°C roasting and water-quenching of BTS yielded various contents of Ce + La in each particle size. In association with this finding, roasting and water-quenching in previous investigations has the same effect on the contents of each grain size of BTS [11,26].

Differences in contents in each grain size of BTS were not only present in valuable oxides, but also in MOO and EMO. Ce + La contents in BTS that have not been processed at all amounted to 1.70%. However, after undergoing several processes, namely roasting, water-quenching, and sieving, the lowest Ce + La contents in the BTS were 1.25% present in -250 mesh BTS particles while the highest ones were 3.03% present in -200 + 250 mesh BTS particles. Since the -200 + 250 mesh BTS-RQS particles had the highest contents of Ce + La but low contents of EMO, the BTS-RQS particles of that size were used as samples in NaOH leaching. Table 2 shows the contents of elements and oxides in both BTS and BTS-RQS.

3.3. NaOH Leaching of BTS-RQS

To see the condition of ions or compounds in the leaching process, the researchers used the Ellingham diagram. In general, the ionic conditions of a chemical element in the Ellingham diagram indicate that the chemical element will dissolve while the conditions of the compound indicate that the element is insoluble. Evaluation through the Ellingham diagram requires a pH value of the solution. In this regard, the pH value of the 8M NaOH solution was calculated using the formula pOH= -logCa\textsubscript{OH}\textsuperscript{-} and pH+pOH=14. These calculations yielded a pH value of 14.903.

The results of 8M NaOH leaching in BTS-RQS are provided in Table 3. This table shows 5.8% Ce + La, 36.48% MOO, and 57.72% EMO. Meanwhile, the overall comparison between the Ce + La, MOO, and EMO contents present in the BTS and those present in the BTS-RQS residues after 8M NaOH leaching is on Fig.2.

### Table 2. The contents of elements and oxides in both BTS and BTS-RQS

| Elements | Content (%) | Content of BTS-RQS (%) at each mesh |
|---------|------------|-------------------------------------|
| Ce      | 1.57       | 3.99  3.54  1.27  3.93  1.01 |
| La      | 0.13       | 0.68  0.60  0.26  1.10  0.24 |
| SiO₂    | 6.56       | 14.4  15.6  4.68  12.89 4.75 |
| TiO₂    | 2.38       | 6.29  6.75  1.82  3.32  1.78 |
| Fe₂O₃   | 2.36       | 6.17  6.60  2.01  4.17  1.97 |
| CaO     | 1.22       | 5.22  5.69  0.03  4.42  - |
| Al₂O₃   | 0.52       | 2.93  3.28  0.24  2.96  - |
| Zr      | 1.33       | 4.65  4.52  1.52  4.05  1.55 |
| Sn      | 1.78       | 6.04  6.39  2.63  7.06  2.93 |
| EMO     | 82.2       | 49.6  47.0  90.2  56.1  85.8 |

### Table 3. The results of characterization of residues from NaOH leaching.

| Element | Residue (%)\(^1\) | Filtrate (ppm)\(^2\) |
|---------|------------------|------------------|
| Ce      | 4.35             | 1.45             |
| La      | 3.23             | 4.07             |
| TiO₂    | 4.07             | 6.49             |
| Zr      | 5.72             | -                |
| Sn      | 57.72            | -                |

\(^1\)XRF characterization  \(^2\)AAS characterization

On Fig.3 (a), the rise in Ce + La contents show that at pH 14.903, cerium is more dominant in the form of CeH\textsubscript{2} and CeO\textsubscript{2}. This means that 8M NaOH leaching only dissolves little cerium. On the other hand, the dominant lanthanum is in the form of LaH\textsubscript{2} and La(OH)\textsubscript{3}, as shown on Fig.3 (b). This implies that 8M NaOH leaching does not dissolve lanthanum. Of these two leachings, the most influential on enhancing Ce + La contents is the dissolution of MOO during NaOH leaching, as shown on Fig. 2 where the extreme decrease occurred in MOO contents, from 82.15% to 57.72%.

The results of AAS characterization of MOO: Fe and Ca (Table 3) show Fe 2 ppm and non-detected Ca. That means that NaOH leaching slightly dissolves Fe and Ca.

Fig.2 shows the increase in all MOO oxides contents. Nevertheless, this rise is not due to the dissolution of MOO. Chronologically, based on the negative value of Gibbs free energy (ΔG) in Table 4, the reactions of MOO to NaOH leaching indicated dissolution. It was signified by a spontaneous reaction. Thus, it concludes that the increase in MOO contents is due to the dissolution of large-scale EMO contents.
As shown on Fig.4 (a), after being leached with HClO$_4$, Ce + La contents were relatively stable even though the concentration of HClO$_4$ was raised. On the other hand, the results of AAS characterization of MOO: Fe and Ca show an increase in Fe and Ca contents. This phenomenon implies that, first, the solubility of Fe and Ca rises as the concentration of HClO$_4$ is increased and, secondly, MOO contents in the residues decline, as shown on Fig. 4 (b).

For the analysis of HClO$_4$ leaching, the pH of HClO$_4$ was calculated first, as shown in Table 5. The evaluation of Ce and La at pH = 0.097, 0.4, and 1 shows Ce in the form of CeH$_2$, CeCl$_{1+a}$, and CeClO$_{4+2a}$, as shown on Fig.5 (a), while La in the form of LaH$_2$, LaCl$_{1+2a}$, and La$_{3+3a}$, as shown on Fig. 5 (b). This implies that Ce and La are massively dissolved.

HClO$_4$ leaching resulted in a decrease in all MOO contents in the residues, as shown on Fig.4 (b). This was signified by a rise in Ca and Fe contents in the filtrates, as shown in Table 6. This condition indicates that HClO$_4$ leaching dissolves Ca and Fe. In general, HClO$_4$ leaching leads to the decrease in the contents of Ce + La and MOO, but causes the rise in EMO contents, as shown on Fig. 6.

### Table 5: The results of pH calculation of HClO$_4$.

| Concentration of HClO$_4$ (M) | pH (pH = -log C$_{H^+}$) |
|------------------------------|--------------------------|
| 0.1                          | 1                        |
| 0.4                          | 0.4                      |
| 0.8                          | 0.097                    |

### Table 4: The $\Delta G$ of MOO dissolution in NaOH.

| No. | Reaction Equation | $\Delta G_{298}^\circ$ (kcal) |
|-----|-------------------|-------------------------------|
| 1.  | SiO$_2$ + 2NaOH = Na$_2$SiO$_3$ + H$_2$O | -21.228                        |
| 2.  | 6TiO$_2$ + 2NaOH = Na$_2$Ti$_6$O$_{13}$ + H$_2$O | -23.582                        |
| 3.  | Fe$_2$O$_3$ + 2NaOH = 2NaFeO$_2$ + H$_2$O | -4.262                         |
| 4.  | CaO + NaOH = / | -8.165                         |
| 5.  | Al$_2$O$_3$ + 2NaOH = 2NaAlO$_2$ + H$_2$O | -5.954                         |
| 6.  | ZrO$_2$ + NaOH = Na$_2$ZrO$_3$ + H$_2$O | Not found from database        |
| 7.  | SnO$_2$ + NaOH = Na$_2$SnO$_3$ + H$_2$O | Not found from database        |
Fig. 6. The contents of Ce+La and EMO as the concentration of HClO$_4$ was raised.

Table 6. The results of AAS characterization of Ca and Fe in the filtrates from HClO$_4$ leaching.

| Concentration of perchloric acid (M) | Calcium (ppm) | Ferro (ppm) |
|-------------------------------------|---------------|-------------|
| 0.1                                 | 3,466.25      | 82.33       |
| 0.4                                 | 3,874.75      | 626.9       |
| 0.8                                 | 4,672.75      | 1,281.6     |

4. Conclusions

Processing BTS with roasting, water-quenching, and NaOH leaching followed by HClO$_4$ to recover cerium and lanthanum, in summary, yields several results as follows:

1. Sieving BTS that has undergone 900°C roasting and water-quenching produces various particle sizes having different Ce + La contents. The optimal Ce+La contents are present in -200 + 250 mesh.

2. The analysis of NaOH dissolution in BTS shows an increase in Ce+La contents due to two factors. First, cerium slightly dissolves in NaOH while lanthanum is insoluble in NaOH and, secondly, almost + 25% EMO dissolves in NaOH.

3. The dissolution of HClO$_4$ leads to a decrease in Ce+La contents since Ce and La are largely soluble in HClO$_4$ as well as MOO. However, the solubility of Ce+La and MOO increases the contents of EMO.

To obtain the optimal contents of cerium and lanthanum, Bangka tin slag is processed by roasting 900°C, water-quenching, and leaching of NaOH, not HClO$_4$.

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