Purification of Cassiterite Mineral Bangka Indonesia by Pyrometallurgy and Hydrometallurgy Methods

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Abstract. The cassiterite mineral is producing mineral of tin. It is widely used in the manufacture of catalysts such as FTO (Fluorine Tin Oxide) glass coatings or as a SnO₂ pigment. Tin is usually used in energy and electronics sector. Cassiterite can be found on the islands of Bangka, Belitung, Kundur, Singkep, Karimun and Kampar. In Indonesia, cassiterite mixed with other minerals such as ilmenite, quartz sand, zircon, rutile, pyrite, calcite, lanthanum and monazite. Those mixtures able to give rise of problems if used as raw chemical materials in tin production. The purifying process of cassiterite is done by pyrometallurgy and hydrometallurgy methods. The XRF and XRD analysis of raw cassiterite show that the main components are Sn and O. The decomposition process is done by mixing cassiterite and kalium sulfate (K₂SO₄) with a ratio of 2:3. The leaching process is performed using KOH to dissolve SnO₂ because the compound is soluble in a strong base. The optimum result is obtained at decomposition temperature 800 °C and time of 4 hours. The intermediate product kalium stannate (K₂SnO₃) is not formed because cassiterite has a structure which may cause some difficulties to react with the salt kalium sulfate (K₂SO₄).

1. Introduction
Indonesia is a rich nation with abundant natural resources such are metallic minerals species, one which is cassiterite included in tin ore (raw sand) in Bangka Island [1]. Cassiterites are widely distributed on the islands of Bangka, Belitung, Kundur, Singkep, Karimun and Kampar [2]. Cassiterite has two types of accumulation, primary and secondary type. The primary type formation is hard rock without weathering process from the source rock and the secondary types is weathered rock type, each forming the alluvial deposit and other associated heavy minerals [7]. Cassiterite (SnO₂) is tin oxide mineral with many possible merits one of which is found at catalyst manufacture (tin chemical), for instance in coating of conductive glass FTO (Flourine Tin Oxide) or as SnO₂ pigments [2]. Cassiterite is natural mineral that can be extracted economically [8]. Tin extraction method depends on the type of the ore itself according to the oxidic or sulfide chemical composition [9]. Extraction method of tin from its ore usually utilized by reducing cassiterite with aqueous inorganic acid [11]. Tin is usually utilized in energy and electronic materials sector. The percentage of tin utilization in the world is shown in Figure 1 [3].
Cassiterite in pure state contains 78.6% of tin, but pure cassiterite is rarely found, it explains the contain varied between 73-75% [10]. Tin metal in nature generally exists as oxide. Its primary sources are cassiterite mineral (SnO$_2$) which in Indonesia is mostly found as alluvial deposits resulted from weathering, erosion and transportation process for a very long time along with some of its associated impurities such as quartz, ilmenite, monazite, rutile and zircon [1]. Various processes have been developed to obtain new valuable materials from cassiterite including a decomposition process of cassiterite using sodium carbonate. Another process is reported in decomposing cassiterite using sodium carbonate with addition of flowing CO/CO$_2$ mixture and solvation in NaOH solution [2].

2. **Experimental**

2.1 **Research Material**
The ingredients are cassiterite powder from Bangka, aquadest, KOH pellets (p.a., Merck), K$_2$SO$_4$ powder (p.a., Merck), Whatman filter paper number 41, tissue and weighing paper.

2.2 **Research Tools**
The tools are X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), carbolite furnace, 47900 type furnace, Radwag analytical balance wps 4000/c/1, accu plate hotplate stirrer, magnetic stirrer, watch glass, thermometer, mortar, spatula, glass stirring rod, ceramic crucible, graphite crucible, beaker, filter funnel, erlenmeyer flask and volumetric flask.

2.3 **Stages of Research**
Cassiterite 30 g and K$_2$SO$_4$ 45 g (2:3) were evenly mixed by stirring. The mixtures were placed into ceramic crucible and decomposed as subsequent treatment. The prepared samples were put into 47900 type furnace. Decomposition process was carried out 9 times using 5 temperature variations ranging from 500-900 °C and 4 time variations (1,2,3,4 hours) of the most optimum temperature. The sample was cooled in furnace to be processed the following day. It was weighed to determine the loss of mass after decomposition process. The results were partly used for leaching process and the rest were analyzed using XRD. Samples 40 g were taken from decomposed results. Leaching process was carried out using KOH solution 2 M for 2 hours at room temperature and stirred using magnetic stirrer proceeded with filtration using two sheets of Whatman filter paper number 41. The filtrate was further proceeded with evaporation while the residue was dried for XRD analysis material. Filtrate was evaporated at temperature 100 °C until it became saturated. The saturated solution was crystallized at temperature of 100-110 °C. The formed crystals were calcined using carbolite furnace at 800 °C for 3 hours and analyzed using XRD. The remaining decomposed samples, leaching residues and the resulting crystals were analyzed using X-Ray Diffraction to determine the intermediate formation of potassium stannate and SnO$_2$. Cassiterite was characterized using XRD and XRF.
3. Results and Discussion

Initially, cassiterite was characterized using XRD and XRF to identify its elements. The XRF analysis results were shown in Table 1, wherein the most abundant element in cassiterite were Sn 57.82% and O 23.39% [2].

Table 1. XRF Analysis Results of Cassiterite

| No | Element | Content (%) | No | Element | Content (%) |
|----|---------|-------------|----|---------|-------------|
| 1  | Sn      | 57.87       | 9  | Ca      | 0.63        |
| 2  | O       | 23.39       | 10 | Mg      | 0.62        |
| 3  | La      | 3.43        | 11 | Al      | 0.52        |
| 4  | Ce      | 3.37        | 12 | Si      | 0.45        |
| 5  | Nd      | 2.18        | 13 | Cl      | 0.37        |
| 6  | Fe      | 1.79        | 14 | Zr      | 0.29        |
| 7  | P       | 1.68        | 15 | S       | 0.11        |
| 8  | Ti      | 1.45        | 16 | Pb      | 0.04        |

Cassiterite was also analyzed using XRD which results were shown in Figure 2 indicating clear and sharp peaks of SnO$_2$ at 20 (degree) of (26.64; 33.94; 38.02; 51.84; 54.84; 61.94; 64.82; 66.04)° [2].

![Diffractogram of Cassiterite](image)

Figure 2. Diffractogram of Cassiterite

The first process is decomposition, decomposition process was aimed to form intermediates of potassium stanate (K$_2$SnO$_3$) by means of added heat under its melting point. The occuring reaction in decomposition process is show in equation 1.

\[
\text{SnO}_2(s) + K_2\text{SO}_4(s) \rightarrow K_2\text{SnO}_3(s) + \text{SO}_3(g)
\]

Cassiterite and potassium sulfate were mixed with a ratio of 2:3. Temperature variations were carried out to determine decomposition effects on the decreasing mass of decomposed sample. The graph of decomposition temperature effects were shown in Figure 3.
Figure 3. Graph of Decomposition Temperature Effects on Decreasing Mass of Decomposed Sample

The percentage of decreasing mass was smaller along with the increasing temperature, however at temperature 900 °C the percentage was increasing because the probability of particles to evaporate during heating process, optimum yield was obtained at temperature 500 °C for its largest percentage 0.70% and optimum temperature of reaction. The small percentage of decreasing mass due to the occurred reaction between SnO$_2$ and K$_2$SO$_4$ was not yet maximum on temperature variations, because SnO$_2$ was an alluvial sedimentary rock that hardly reacted with salt. Moreover, decomposition process was carried out in atmosphere contained air rather than atmosphere contained CO/CO$_2$ mixture [4]. The results of decreasing mass from decomposed sample were shown in Table 2 and calculated using equation 2.

\[
\text{Decreased mass} = \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \times 100\%
\]  

Table 2. Results of Decreasing Mass from Decomposed Sample

| Sample  | Initial Mass (g) | Final Mass (g) | Decreased Mass (%) |
|---------|------------------|----------------|--------------------|
| KS-500-3| 75.53            | 75.00          | 0.70               |
| KS-600-3| 75.00            | 74.81          | 0.25               |
| KS-700-3| 75.00            | 74.84          | 0.21               |
| KS-800-3| 75.00            | 74.9           | 0.13               |
| KS-900-3| 75.00            | 74.81          | 0.25               |

The resulting decomposed sample was characterized using XRD to determine newly formed absorption patterns after decomposition process with temperature variations. The diffractogram of decomposed sample was shown in Figure 4.
The diffractogram displayed yield of diffraction patterns from decomposition process using temperature variations of 500 °C - 900 °C, they were matched toward cassiterite’s diffraction pattern and devoid of new pattern. Temperature variations solely affected the diffraction intensity of SnO₂ and K₂SO₄. The intensity of SnO₂ diffraction decreased at 2θ (degree) of (26.8; 34.15; 52.02 and 54.9)° and increased at temperature 800 °C. In contrast to SnO₂, the intensity of K₂SO₄ increased at 2θ (degree) of (30.9; 43.55 and 58.1)° then decreased at temperature 800 °C. It could be concluded that after the reaction underwent decomposition process there were none of new phase formed. Temperature 800 °C in this study was the optimum decomposition temperature since at that condition the sample had the highest SnO₂ and least K₂SO₄ content. Another study mentioned the optimum decomposition temperature of SnO₂ and Na₂CO₃ was 875 °C in atmosphere contained CO/CO₂ mixture [5]. Contents of SnO₂ and K₂SO₄ from the decomposed samples were shown in Table 3.

Table 3. Contents of Decomposed Samples

| Sample  | Content (%) | GOF Value |
|---------|-------------|-----------|
|         | SnO₂        | K₂SO₄     |           |
| KS-500-3 | 50.5        | 48.2      | 3.57      |
| KS-600-3 | 50.2        | 49.0      | 2.19      |
| KS-700-3 | 49.1        | 50.4      | 2.02      |
| KS-800-3 | 54.0        | 43.3      | 2.33      |
| KS-900-3 | 44.4        | 50.1      | 2.15      |

Effect of decomposition temperature variations on leaching process was identified from the solubility of decomposition sample. The leaching process was carried out using KOH solution to dissolve SnO₂ as it could be dissolved in a strong base. The resulting filtrate was evaporated and crystallized to form pure SnO₂ crystals while the residue was characterized using XRD. Figure 5 showed graph of the effect of decomposition temperatures on solubility of decomposed sample.
Figure 5. Graph of the Effect of Decomposition Temperatures on Solubility of Decomposed Sample

The leaching optimum temperature was 800 °C, as it had the biggest solubility 20.225%. At temperature 900 °C the solubility decreased possibly because the small amount of SnO$_2$ was formed during decomposition process. The solubility datas of affected sample by decomposition temperature were shown in Table 4 and calculated using equation 3.

\[
\text{Solubility} = \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \times 100\%
\]  

(3)

Table 4. Solubility Percentage of Decomposed Samples

| Sample  | Initial Mass (g) | Final Mass (g) | Solubility (%) |
|---------|------------------|----------------|----------------|
| KS-500-3| 40               | 32.52          | 18.7           |
| KS-600-3| 40               | 32.9           | 17.75          |
| KS-700-3| 40               | 32.05          | 19.88          |
| KS-800-3| 40               | 31.91          | 20.23          |
| KS-900-3| 40               | 32.36          | 19.1           |

Solubility percentage of decomposed sample was low, as SnO$_2$ in the decomposed sample only dissolved partially. The residue from leaching was characterized using XRD to indentify its contents of unsolved SnO$_2$ and find out new diffraction patterns after leaching process using KOH. Diffractogram of residue from leaching process at decomposition temperatures of 500 °C and 800 °C was shown in Figure 6.

Figure 6. Diffractogram of Residue From Leaching Process (A) KS-500-3 and (B) KS-800-3
Diffractogram displayed that the diffraction pattern of residue had the same pattern and gave no indication of new patterns. Those diffractogram only showed increasing intensity of SnO$_2$ and decreasing intensity of K$_2$SO$_4$ due to temperature rise. The intensity of SnO$_2$ diffraction pattern increased at 2$\theta$ (degree) of (26.8; 34.1; 38.2; 51.9 and 55.2$^\circ$) while intensity for K$_2$SO$_4$ decreased at 2$\theta$ (degree) of (31.1 and 48.3$^\circ$). Contents of SnO$_2$ and K$_2$SO$_4$ in residue product of leaching process were shown in Table 5.

Table 5. Contents of Residue Product from Leaching Process

| Sample | SnO$_2$ (Content (%)) | K$_2$SO$_4$ (Content (%)) | GOF Value |
|--------|-----------------------|---------------------------|-----------|
| KS-500-3 | 34.2                  | 64.2                      | 3.39      |
| KS-800-3 | 39.8                  | 59.3                      | 2.61      |

Content of SnO$_2$ in samples KS-500-3 and KS-800-3 after decomposition process in Table 3 were 50.5% and 54.00% respectively while after underwent the leaching process they decreased to 34.2% and 39.8% as shown in Table 5.

Time variations were applied when decomposition process was reaching temperature 800 °C since it was the optimum decomposition temperature with the highest SnO$_2$ content and solubility after leaching process. Effects of decomposition time on decreasing mass of decomposed sample were shown in Figure 7.

**Figure 7.** Graph of Effect on Decreasing Mass of Decomposed Sample

The optimum decomposition time was 3 hours with the highest decreasing mass percentage 0.13%. Following the optimum time, percentage on decreasing mass was lessening since its reaction ran suboptimally. The decreasing mass datas were shown in Table 6 and calculated using equation 4.

\[
\text{Decreased mass} = \left(\frac{\text{initial mass} - \text{final mass}}{\text{initial mass}}\right) \times 100\%
\]  

Table 6. Results of Decreasing Mass of Decomposed Sample

| Sample | Initial Mass (g) | Final Mass (g) | Decreased Mass (%) |
|--------|-----------------|----------------|-------------------|
| KS-800-1 | 75             | 74.97          | 0.04              |
| KS-800-2 | 75             | 74.93          | 0.09              |
| KS-800-3 | 75             | 74.9           | 0.13              |
| KS-800-4 | 75             | 74.97          | 0.04              |

A relatively small percentage result was possible because of the non-optimal decomposition reaction between cassiterite and potassium sulfate.
Decomposition time affected solubility in leaching process. The longer decomposition time, the greater solubility of decomposed products. Temperatures at leaching process also affected solubility [6]. The graph of the effects of decomposition time on solubility of decomposed samples was shown in Figure 8.

![Graph of the Effect of Decomposition Time on Solubility of Decomposed Sample](image)

The optimum time from leaching process was 4 hours with solubility percentage 20.95%. These relatively small solubility result was probably caused by too little time on stirring process, thus the solution had saturated. Moreover, leaching process was carried out at room temperature. Previous research mentioned the optimum temperature of leaching tin (Sn) using NaOH 1 M at temperature 90 °C for 2 hours resulted in percentage 62.4% [6]. Effects of decomposition time on solubility were shown in Table 7 and calculated using equation 5.

$$\text{Solubility} = \frac{{\text{initial mass} - \text{final mass}}}{{\text{initial mass}}} \times 100\%$$  \hspace{1cm} (5)

| Sample | Initial Mass (g) | Final Mass (g) | Solubility (%) |
|--------|-----------------|----------------|----------------|
| KS-800-1 | 40              | 32.71          | 18.23          |
| KS-800-2 | 40              | 32.51          | 18.73          |
| KS-800-3 | 40              | 31.91          | 20.23          |
| KS-800-4 | 40              | 31.62          | 20.95          |

The filtrate from leaching process was evaporated to remove H₂O at temperature 100 °C until it became saturated solution. Those saturated solution was crystallized at temperature of 100-110 °C to evaporate the still existing water molecules to obtain crystals. Its form was hydrate and hygroscopic, hence the calcination at temperature 800 °C for 3 hours using calbolite furnace was conducted. White and non-hygroscopic crystals which were produced after calcination process possibly were purer cassiterite mineral crystals.

4. Conclusion

The conclusions from the research results are the optimum temperature of cassiterite purification was obtained at 800 °C because decomposed sample had the highest SnO₂ content and highest solubility 20.95% during leaching process and the optimum time in cassiterite purification process was obtained at 4 hours with potassium stannate intermediate expectedly not to be yielded through temperature variations of 500-900 °C since the process of forming K₂SnO₃ was accompanied by cassiterite’s (SnO₂) inability to react with salt (K₂SO₄) because of its form as rock alluvial sediment which structure caused difficulty to react with salt.
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