The Formation of Sodium Stannate from Mineral Cassiterite by the Alkaline Decomposition Process with Sodium Carbonate (Na$_2$CO$_3$)

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Abstract. Extraction of cassiterite using alkaline decomposition of sodium carbonate (Na$_2$CO$_3$) has been studied. Cassiterite (SnO$_2$) is a mineral ore that contains tin (Sn) about 57.82 wt% and impurities like quartz, ilmenite, monazite, rutile and zircon. The initial step for the process was to remove the impurities in cassiterite through washing and separation by a high magnetic separator (HTS). The aim of this research is to increase the added value of cassiterite from local area Indonesia that using alkaline decomposition to form sodium stannate (Na$_2$SnO$_3$). The result shows that cassiterite from Indonesia can form sodium stannate (Na$_2$SnO$_3$) which soluble with water in the leaching process. The longer the time for decomposition, the more phases of sodium stannate that will be formed. Optimum result reached when the decomposition process was done in 850 ºC for 4 hours with a mole ratio Na$_2$CO$_3$ to cassiterite 3:2. High Score Plus (HSP) was used in this research to analyze the mass of sodium stannate (Na$_2$SnO$_3$). HSP analysis showed that mass of sodium stannate (Na$_2$SnO$_3$) is 70.3 wt%.

1. Introduction

One of minerals that abundantly available in Indonesia is cassiterite, the raw material for tin (Sn). It is widely spread on the islands of Bangka, Belitung, Kundur, Singkep, Karimun and Kampar [1]. Mineral cassiterite has a chemical formula SnO$_2$ which mainly consisting of tin (Sn) and oxygen (O) [2]. Cassiterite ore has been processed commercially through pyrometallurgy to produce metal or high purity tin ingot. The energy extraction process using high temperature (melting) and reducing agents such as anthracite (coal) made using reverberatory furnace [1]. Lead optimization efforts from upstream to downstream is prospective to do that is by turn lead into new compounds which have a higher economic value, such as tin dioxide as a catalyst.

Various processes have been developed to obtain valuable materials from the mineral cassiterite, the process of which is a) the decomposition process cassiterite with sodium carbonate at 900 ºC for 120 minutes, which then dissolved using 25% HCl to eliminate the main impurity elements, including Fe, As, S, Pb, and Sb. From the results of these studies found that cassiterite (SnO$_2$) slightly react with impurities during the decomposition process and does not dissolve in hydrochloric acid significantly [3]. b) Concentrate cassiterite is decomposed with sodium carbonate (Na$_2$CO$_3$) were then fed with gas mixed CO/CO$_2$ and dissolved into a solution of NaOH, then filtered to obtain the filtrate which is rich

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in sodium stannat and will dissolve in the water when done heating and crystallization, from the research results obtained leaching efficiency of 85.6% and the product had a purity of 95.8% SnO\textsubscript{2}, with optimal conditions the decomposition temperature of 875 °C, 15% CO gas content, the decomposition time 15 minutes, mole ratio Na\textsubscript{2}CO\textsubscript{3}/cassiterite 3: 2, leaching temperature of 40 °C, leaching time of 60 minutes, stirring speed of 300 rpm and the ratio L/S 4 cm\textsuperscript{3}/g [4].

c) The process of extracting tin from tin concentrate using low levels of HCl 150 g/L, 2 hours, 35 °C which is able to separate the iron up to 99.4%, but the process of decomposition continued with a mixture of 55% Na\textsubscript{2}CO\textsubscript{3}, 12% NaOH, 30% residue leaching and 3% of coal at a temperature of 870 °C. Tin recovery results obtained at 99.66% [5].

The alternative process that applied in this research is extracted through decomposition with sodium carbonate to produce sodium stannat, where sodium stannat can be dissolved in water [4-6] to obtain filtrate enriched with tin (Sn). The mole ratio of Na\textsubscript{2}CO\textsubscript{3} to cassiterite, temperature and reaction time are critical parameters for the sodium stannat phase formation of the yield value of the final product as a tin dioxide (SnO\textsubscript{2}). In this paper, we report results on the effect of mole ratio Na\textsubscript{2}CO\textsubscript{3} to cassiterite, temperature and reaction time to the process of formation of sodium stannat compounds.

2. Experimental

2.1. Materials and reagents

The raw material cassiterite for experiment was received from Bangka Island-Indonesia. Another raw materials for experiment were an analytical grade sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}). The detailed chemical composition of the cassiterite was examined by XRF (X-Ray Fluorescence) and the analytic results are listed in Table 1.

| No. | Element | Percentage (% wt) | No. | Element | Percentage (% wt) |
|-----|---------|-------------------|-----|---------|-------------------|
| 1.  | Sn      | 57.82             | 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              |

2.2. Experimental Methods

The prior step was grinding cassiterite to particle size -100 mesh and characterizing with X-Ray Diffraction (XRD), and XRF (X-Ray Fluorescence) apparatus. Then second step was decomposed cassiterite using various sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) with the mole ratio is 1:1, 3:2, and 2:1 in atmospheric conditions at various temperature of 800, 850, 870 and 900 °C for 2, 3 and 4 hours. Finally, product of decomposed was characterized using XRD analysis. Experiments were performed in a carbolyte furnace using graphite crucibles. The concentrated Na\textsubscript{2}CO\textsubscript{3} and cassiterite were then homogeneously mixed in graphite crucibles and put into the carbolyte furnace when the temperature reached the present value, with free access of air. The temperature of the carbolyte furnace was controlled by a programmable temperature controller.

The reaction of cassiterite with sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) forms sodium stannate (Na\textsubscript{2}SnO\textsubscript{3}) and could be described as follows [4]:

\[
\text{SnO}_2(s) + \text{Na}_2\text{CO}_3(s) \rightarrow \text{Na}_2\text{SnO}_3(s) + \text{CO}_2(g) \quad (1)
\]
3. Results and discussion

3.1. The Characteristic of Bangka Cassiterite

A chemical composition of Bangka Cassiterite was analyzed by using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD). The result is presented at Table 1 and Fig. 1, which shows that the dominant compound exist Tin (Sn) and Oxigen (O). Another compounds which are also exist in cassiterite from Bangka Island are La, Ce, Fe, Ti, Si, Mg, Ca, but their quantities are lower than Sn.

This result of chemical analysis are in a good agreement with the result of phase identification by using XRD at Fig. 1, which showed that the dominant phase exist in cassiterite from Bangka Island is tin dioxide (SnO$_2$), the diffraction pattern in accordance with PDF 2 No. 01-0657. The X-ray diffractograms of cassiterite Bangka Indonesia showed sharp diffraction peak intensity at 2θ of 26.64°, 33.94°, 38.02°, 51.84°, 54.84°, 61.94°, 64.82° and 66.04°. La$_2$Sb and CeSe phase was also found in Bangka cassiterite, but their X-ray diffraction intensities were relatively lower than the X-ray diffraction intensities of tin dioxide (SnO$_2$). Another phases were not detected due to their quantities were relatively lower as it is shown by the result of chemical analysis by using X-Ray Fluorescence (XRF) at Table 1.

![Figure 1. XRD pattern of cassiterite](image)

3.2. Effect of mole ratio Na$_2$CO$_3$ to cassiterite

The result of X-ray diffraction of the decomposed cassiterite at Fig. 2 shows that sodium stannat (Na$_2$SnO$_3$) phase was found at cassiterite decomposition products. This result of phase identification same with the results of Zhang, Y [4] and Bunnakkha, C [6] experiments. Fig. 2 also shows that when the mole ratio of Na$_2$CO$_3$ was increased up to 2 : 1, the X-Ray diffraction peaks intensities for cassiterite decreases and intensities for sodium stannat increases are unsignificantly changed. This result of experiment shows that the decomposition reaction of cassiterite with Na$_2$CO$_3$ will be more effective when the mole ratio of Na$_2$CO$_3$ increases from 1 : 1 to 2 : 1.

The similar tendencies were found by Zhang, Y et.all [4] during decomposition of cassiterite by concentrated sodium carbonate (Na$_2$CO$_3$). He found that when the mole ratio of Na$_2$CO$_3$ were increased rapidly until it tends to be balanced at the Na$_2$CO$_3$ to cassiterite mole ratio higher than 1.50. Thus, Na$_2$CO$_3$ to cassiterite mole ratio of 1.50 is the most favorable value.
Table 2 shows the results of quantitative or weight percent of each phase were calculated by the method High Score Plus, where there is an increase in weight % Na₂SnO₃ phase of 8.1 wt % to 9.3 wt %. The greater the amount of Na₂CO₃ is added into the cassiterite will lead to increased formation of sodium stannat phase.

### Table 2. Quantitative Analysis of phase in various concentrations

| Mole ratio | Sample  | Cassiterite (wt %) | Na₂SnO₃ (wt %) | Natrite (wt %) | GOF |
|------------|---------|---------------------|----------------|---------------|-----|
| 1:1        | A-850-2 | 34.6                | 8.1            | 57.3          | 1.52|
| 3:2        | B-850-2 | 15.7                | 8.4            | 75.9          | 1.38|
| 2:1        | C-850-2 | 10.9                | 9.3            | 79.8          | 1.53|

3.3. Effect of Reaction Time

The effect of reaction time on the formation of sodium stannat phase during decomposition process with Na₂CO₃ were observed to the -100 mesh cassiterite that was decomposed with mole ratio Na₂CO₃ to cassiterite : 3:2, temperature 850 °C for decomposition time 2 hours, 3 hours, and 4 hours respectively. The result is presented at Fig. 3 which shows that the intensities of sodium stannat phase started to forms at decomposition time 2 hours, and their intensities increases significantly when decomposition time was extended up to 4 hours. Table 3 shows the results of quantitative or weight percent of each phase were calculated by the method High Score Plus, where there is an increase in weight % Na₂SnO₃ phase of 8.4 wt % to 70.3 wt %. The longer the time given in the decomposition process, reaction of sodium stannat phase formation that occurs will be increase [6]. So for this experiment, the optimum time of decomposition seen at 4 hours.

### Table 3. Quantitative Analysis of phase in various reaction time

| Time (hour) | Sample  | Cassiterite (wt %) | Na₂SnO₃ (wt %) | Natrite (wt %) | GOF |
|-------------|---------|---------------------|----------------|---------------|-----|
| 2           | B-850-2 | 15.7                | 8.4            | 75.9          | 1.38|
| 3           | B-850-3 | 4.8                 | 29.1           | 66.0          | 1.41|
| 4           | B-850-4 | 0.8                 | 70.3           | 28.9          | 1.45|
3.4. Effect of Temperature

The effect of temperature on the formation of sodium stannat phase during decomposition process of cassiterite with Na$_2$CO$_3$ were observed to the -100 mesh cassiterite by using mole ratio Na$_2$CO$_3$ to cassiterite : 3:2, at decomposition temperatures 800 °C up to 900 °C, for 4 hours. The result of decomposition reactions were then analyzed by using XRD. Fig. 4 shows the result of X-Ray diffraction analysis to the decomposed cassiterite. From the result of analysis by using XRD at Fig. 4 and Table 4, it is shown that Na$_2$SnO$_3$, cassiterite and Na$_2$CO$_3$ were found at cassiterite decomposition products. The X-ray intensities of cassiterite increased and intensities of sodium stannate decreased when the decomposition temperature were increased from 850 °C to 900 °C and so sodium stannate phase optimum was found at decomposition temperatures 850 °C.

At a lower temperature of 800 °C phase sodium stannat unobserved. This is evident from the results of TG/DTA in cassiterite + Na$_2$CO$_3$ that the temperature required for the endothermic reaction occurs at temperatures of 830-880 °C, in other words sodium stannate formation occurs at this temperature. The same is done on previous research that Zhang, Y [4] and Bunnakkha, C [6] where the decomposition temperature used in research that is 870 °C with decomposition recovery yield of 90.66 % and 85.6 %.

**Table 4.** Quantitative Analysis of phase in various temperature

| Temperature °C | Sample   | Cassiterite (wt %) | Na$_2$SnO$_3$ (wt %) | Natrite (wt %) | GOF  |
|---------------|----------|--------------------|----------------------|----------------|------|
| 800           | B-800-4  | 18.0               | -                    | 82.0           | 1.35 |
| 850           | B-850-4  | 0.8                | 70.3                 | 28.9           | 1.45 |
| 870           | B-870-4  | 3.7                | 59.3                 | 37.0           | 1.37 |
| 900           | B-900-4  | 4.2                | 55.6                 | 40.1           | 1.46 |
4. Conclusion
It could be concluded that the main element of cassiterite was 57.82% Sn and others were 42.18% associated elements. The result of XRD analysis showed that the major minerals of cassiterite were indexed as tin dioxide (SnO₂) phase. It is concluded that Bangka cassiterite could be decomposed with sodium carbonat and can form sodium stannate (Na₂SnO₃) which soluble with water in leaching process and optimum result reached when the decomposition process was done in 850 °C for 4 hours with mole ratio Na₂CO₃ to cassiterite 3:2, with the percentage mass of sodium stannate (Na₂SnO₃) is 70.3 wt%.

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