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SYNTHESIS OF SODIUM STANNATE USING ALKALINE PRESSURE LEACHING PROCESS

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ABSTRACT

Sodium stannate has numerous applications, including electroplating, tin alloy, catalysts, precursor to flame retardants, and also can be used as solid electrolytes and electrode materials in emerging battery systems. The primary method for producing sodium stannate typically involves the reaction between tin metal and sodium hydroxide solution. However, the procedure exhibited several limitations, such as high energy consumption, a long process flow for the production of metallic tin, as well as the release of potentially hazardous gases. Therefore, the present study focused on synthesizing sodium stannate from cassiterite minerals through alkaline pressure leaching, followed by crystallization. The main aim of this study was to examine the effect of various leaching process parameters, such as sodium hydroxide concentration, leaching temperature, and leaching time on the improvement of tin dissolution. The results showed that the alkaline pressure leaching process can successfully produce sodium stannate from the cassiterite mineral. The optimum parameters for alkaline pressure leaching to produce sodium stannate from cassiterite have been determined: temperature of 150°C, sodium hydroxide concentration of 4 mol/L, and duration of 240 minutes.

Keywords: Cassiterite, Sodium Hydroxide, Sodium Stannate, Pressure Leaching, Alkaline Leaching

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INTRODUCTION

The global reserves of tin (Sn) are currently estimated to be approximately 4,600,000 tons, with Indonesia holding the greatest share of reserves at 800,000 tons. In 2021, the global production of tin reached 305,000 tons, exhibiting an average annual growth rate of roughly 2% over the past decade.[1] More than 80% of tin metal is extracted through a pyrometallurgical route, which involves smelting and refining.[2] Tin possesses notable utility in many different fields, including soldering, alloy formation, electroplating, and chemical processing. Tin can also be employed in the form of chemical compounds, such as stannic oxide, stannous fluoride, sodium stannate, and others. Sodium stannate ($Na_2SnO_3.3H_2O$) is highly desirable in several industries due to its versatile applications, including electroplating, tin alloy manufacture, catalyst utilization, and its role as a precursor to flame retardants.[3–7] Other applications, including solid electrolytes and electrode materials in emerging battery systems, have also been observed in recent studies.[8–10] The global demand for sodium stannate has experienced a notable increase during the past ten years that can be attributed to the substitution of the regular flame retardant antimony trioxide (Sb_2O_3) by zinc stannate, which is typically derived from sodium stannate and zinc compound via hydrometallurgical processes.[11,12]

The primary method for producing sodium stannate typically involves the reaction between tin metal and sodium hydroxide solution. The procedures exhibited several limitations, such as high energy consumption and a long process flow for producing metallic tin, as well as the release of potentially hazardous gases (NO_x or NH_3) from the oxidizers.[13,14] In light of these considerations, several researchers

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attempted to synthesize sodium stannate using cassiterite as raw material.[15,16] Some secondary tin-containing resources were also utilized in the production of sodium stannate. The recovery process of tin to produce sodium stannate encompasses two main routes: pyrometallurgical and hydrometallurgical. Tin can be transformed into soluble sodium stannate through a process with the addition of either sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3). In their respective studies, Liu employed sodium carbonate to roast tin anode slime, while Wu utilized sodium hydroxide for the roasting of lead refining dross.[17,18] Several researchers also performed alkaline pressure leaching procedures utilizing tin anode slime, a metal powder derived from scrap printed circuit boards (PCB), and Sn-Cu bearing residue to produce sodium stannate.[2,19,20] The current investigation focused on the process of synthesizing sodium stannate from cassiterite minerals through alkaline pressure leaching, followed by crystallization. The present study aimed to evaluate the effect of various leaching process parameters, namely sodium hydroxide concentration, leaching temperature, and leaching time on the improvement of tin dissolution. The synthesis of sodium stannate was completed by the crystallization process.

EXPERIMENTAL

Material and Methods

Cassiterite, used as raw material, was sourced from Bangka, Indonesia. For the leaching studies, a solution was prepared using the analytical grade of sodium hydroxide (NaOH) from Merck and deionized water. Before use, the cassiterite material was thoroughly mixed, and the samples were collected using the coning and quartering techniques for analysis and pressure-leaching studies. The chemical compositions of cassiterite were determined using XRF (X-ray Florescence Spectrometer), and the result is presented in Table-1. The results revealed that the cassiterite mineral used in this investigation mostly consists of tin, along with trace quantities of various impurities, including lanthanum (La), cerium (Ce), neodymium (Nd), iron (Fe), phosphorus (P), titanium (Ti), calcium (Ca), magnesium (Mg), aluminum (Al), silicon (Si), zirconium (Zr), sulfur (S), and lead (Pb). Preliminary characterization of the Bangka cassiterite mineral by XRD (X–ray Diffraction) analysis is depicted in Fig.-1. It can be seen that the substance is mostly composed of SnO_2 alongside TiO_2.

General Procedure

The leaching process was carried out using a 100 ml autoclave where for each test, a quantity of 20 grams of cassiterite mineral was initially mixed with a 60 mL volume of sodium hydroxide solution with a predetermined concentration that was varied between 3 mol/L to 5 mol/L. Subsequently, the mixture was subjected to heating until it reached the predetermined temperatures that were varied between 80°C to 150°C.

Table-1: Chemical Composition of the Cassiterite Used in This Research

Element	Weight Percent (%)
Sn	57,82
O	23,39
La	3,43
Ce	3,37
Nd	2,18
Fe	1,79
P	1,68
Ti	1,45
Ca	0,63
Mg	0,62
Al	0,52
Si	0,45
Cl	0,37
Zr	0,29
S	0,11
Pb	0,04

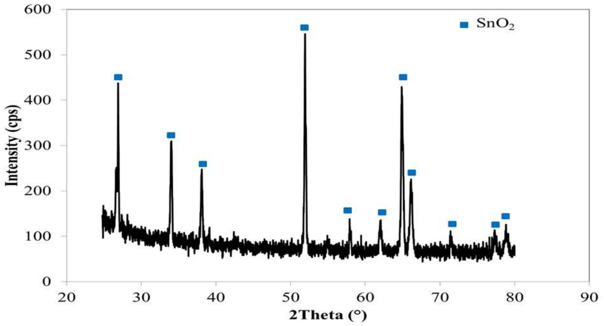

Fig.-1: XRD Diffractogram of Cassiterite Mineral

After 3 hours, the autoclave was promptly cooled and subsequently depressurized. The chemical reaction that occurred during the leaching process is given as follows:

$SnO_2 + 2NaOH = Na_2SnO_3 + 2H_2O$ (1)

The slurry was further subjected to a liquid-solid separation, while the filtrate solution was subjected to an evaporation process to obtain sodium stannate.

Detection Method

An Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) was used for conducting element concentration analysis in leaching filtrates. The resulting product was characterized using XRD and scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). XRD analysis was performed to identify the crystalline composition, while SEM-EDS was used to characterize the microstructures of the product.

RESULTS AND DISCUSSION

Effect of Sodium Hydroxide Concentration

The influence of varying sodium hydroxide concentrations, ranging from 3 mol/L to 5 mol/L, was investigated. This investigation was conducted under specific leaching conditions, including a leaching duration of 3 hours and a leaching temperature of 120°C. The results are depicted in Fig.-2. The observed trend indicates that there was an increase in the concentration of Sn in the filtrate solution from 6,948 ppm to 13,273 ppm as the concentration of sodium hydroxide was increased from 3 mol/L to 4 mol/L. Nevertheless, the concentration of Sn showed a decline to 11,403 parts per million (ppm) and 10,370 ppm as the concentration of sodium hydroxide was further increased to 4.5 mol/L and 5 mol/L, respectively. The observed phenomenon might likely be attributed to the negative influence of an excessive concentration of sodium ions (Na^+) on the dissolving process of tin. Therefore, a sodium hydroxide concentration of 4 mol/L is regarded as the most optimal amount.

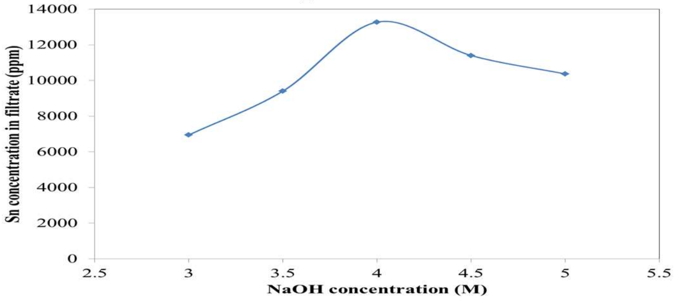

Fig.-2: Effect of Sodium Hydroxide Concentration on Tin Dissolution

Effect of Leaching Temperature

The effect of varying leaching temperatures on the effectiveness of Sn dissolution was examined within a temperature range of 80°C to 150°C. The experiments were conducted using a leaching solution consisting of 3 mol/L sodium hydroxide concentration, with a leaching duration of 3 hours. The results are shown in Fig.- 3. As can be seen, the concentration of Sn in the filtrate solution increased from 4,387 ppm to 7,865 ppm when the leaching temperature was increased from 80°C to 150°C. Figure-3 shows that the reaction is significantly influenced by the leaching temperature. High temperatures have the potential to accelerate the motion of ions, hence promoting chemical reactions.[2] Furthermore, the Pourbaix diagram for the Sn–H_2O system indicates that it is challenging to dissolve Sn in an alkaline solution at room temperature. Nevertheless, with increasing temperature, the stability area of SnO_3^{2-} expands, resulting in enhanced solubility of Sn.[20] Nevertheless, higher temperatures can increase energy consumption. Hence, it is necessary to determine the optimal temperature conditions for alkaline pressure leaching, and a leaching temperature of 150°C is regarded to be the most favorable value.

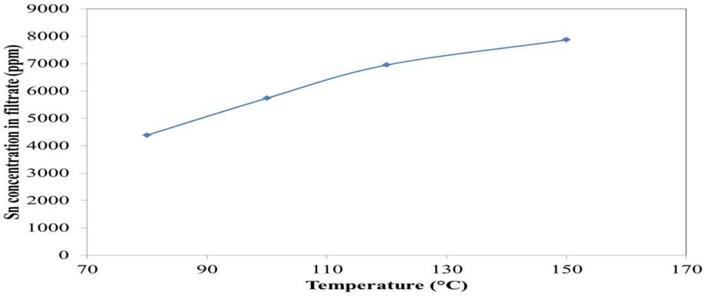

Fig.-3: Effect of Temperature on Tin Dissolution

Effect of Leaching Duration

The effect of several leaching durations, ranging from 30 minutes to 240 minutes, on the effectiveness of Sn leaching was investigated. This investigation was conducted under specific leaching circumstances, including a leaching temperature of 120°C and a sodium hydroxide concentration of 3 mol/L. The results can be seen in Fig.-4. The observed trend indicates that there was an increase in the concentration of Sn in the filtrate solution from 5,314 ppm to 7,371 ppm as the leaching duration was extended from 30 minutes to 240 minutes. The data presented in Fig.-4 demonstrates that the reaction between stannic oxide and sodium hydroxide is rapid. Further increasing the time, the contact period between sodium hydroxide and sodium stannate was prolonged, leading to an increase in the dissolution of tin. Hence, the optimal parameters for alkaline pressure leaching emerged as (i) a temperature of 150°C, (ii) a sodium hydroxide concentration of 4 mol/L, and (iii) 240 minutes. Following the alkaline pressure leaching process, a liquid-solid separation procedure was carried out on the slurry. The filtrate solution was subjected to an evaporation process to obtain sodium stannate. The crystalline composition of the product was analyzed by XRD, as shown in Fig.-5. The microstructure of the product was also analyzed using SEM-EDS, as depicted in Fig.-6.

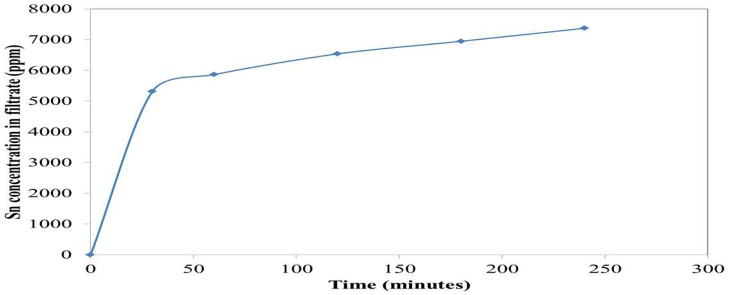

Fig.-3: Time Influence on Tin Dissolution

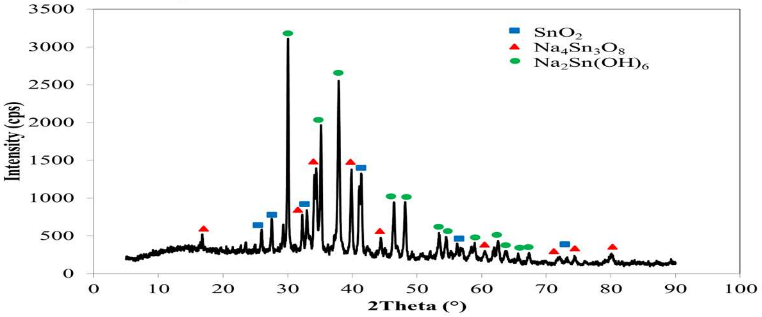

Fig.-4: XRD Diffractogram of the Sodium Stannate Product

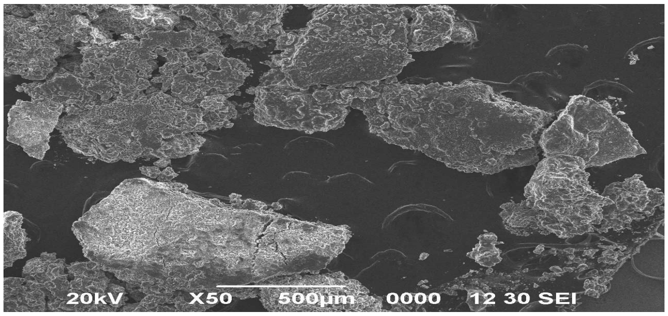

Fig.-5: SEM Image of the Sodium Stannate Product

Compared with Fig.-1, the peaks that represent TiO_2 were not detected in Fig.-5, while the presence of sodium stannate as $Na_4Sn_3O_8$ and $Na_2Sn(OH)_6$ were observed in the resulting product. This finding demonstrates that TiO_2 and some SnO_2 could not be extracted by alkaline pressure leaching. The tetragonal crystal system is observed in the crystalline structure of SnO2. The alkaline pressure leaching method using sodium hydroxide disrupted Sn-O bonds present in SnO_2, resulting in the formation of sodium stannate as $Na_4Sn_3O_8$ with cubic crystal system and as $Na_2Sn(OH)_6$ with trigonal crystal system. Fig.-6 shows the SEM image of sodium stannate product morphology was an irregular shape, with the particles exhibiting agglomeration.

CONCLUSION

Based on the investigation, it can be concluded that sodium stannate could be successfully produced from cassiterite minerals using alkaline pressure leaching followed by crystallization processes. As indicated by the experimental results, extractions of tin are significantly influenced by several parameters, namely the concentration of sodium hydroxide, leaching temperature, and leaching time. The optimal parameters for alkaline pressure leaching to produce sodium stannate from cassiterite have been found as follows: (i) temperature of 150°C, (ii) sodium hydroxide concentration of 4 mol/L, and (iii) 240 minutes. The filtrate solution underwent a crystallization process to acquire sodium stannate. The XRD analysis result has revealed that the stannic oxide was transformed into sodium stannate.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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