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Optimization on the purification of cassiterite from low-grade cassiterite concentrate

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Abstract. Optimization on the purification of cassiterite from low-grade cassiterite concentrate has been successfully done. The concentrate used came from the mine site in the Delas area, Bangka Island with an element content of Sn was 31.60% wt and the impurity phases including zircon, ilmenite, quartz, hematite, and monazite. The purification process consists of two steps: mechanical-magnetical separation and acid leaching. The mechanical-magnetical separation step started by color separation (bright sand removal) and removed the magnetic elements of the concentrate subsequently. The content of the Sn element in acid leaching residue increased significantly was up to 90.28% with cassiterite as the dominant phase. The X-ray diffraction (XRD) revealed that the impurity phase of the filtrate after crystallization in all varying pH consists of cassiterite, ilmenite, and ammonium chloride. The solubility of cassiterite concentrate in the acid leaching process is very low at 4.4%, this indicates that the Sn element is difficult to decompose under these conditions.

1. Introduction

Cassiterite minerals are tin ores which can be found in rock or alluvial deposits. The distribution of this mineral extends from the Malacca peninsula to the Sunda Land and West Kalimantan, known as the Tin Belts area. Bangka Island is one of the regions located in the Tin Belts area and the location of the largest tin mines in Indonesia. This cassiterite mineral is processed into commercial products as tin bars with high purity. To be able to become a commercial product, the mineral cassiterite will be melted at high temperatures ($>1200^{\circ}$C) to reduce cassiterite to tin metal [1,2]. Cassiterite to be melted must have a high level of purity. This is because it will affect the quality of the tin metal produced. Impurities such as iron will melt together with tin during the melting process and will be difficult to separate if it has formed a stable tin-iron alloy [1]. The impact of the next process will be difficult and requires more energy consumption so operational costs will become more expensive [3].

Cassiterite is one of the functional materials widely used in the development of renewable energy, one of which is as a photovoltaic device for solar cells. The design of photovoltaic devices integrated with energy storage systems is the basis for the development of transparent conducting oxide (TCO) materials. This material is a transparent conductive oxide layer that can conduct electrical charges properly. Of all the types of TCO used, the most developed cassiterite-based TCO. This is because SnO_2 has good mechanical resistance and chemical stability and extensive decomposition ability on the surface of the TCO material [4]. To improve its conductivity it can be doped using fluorine (FTO) or indium (ITO) [5]. This is because the presence of dopant will form a

defect in the process of sintering the oxide layer on the substrate at 400-5000ºC as a solar cell body where the TCO layer and counter electrode are decomposed [6].

Development of cassiterite purification methods has been carried out including such as flotation, comminution, classification, gravity concentration, hydrometallurgical separation, microwave pre-treatment, leaching and others [1,7–9]. The application of purification method depends on the levels and types of impurities in the concentrate. The right purification method can lead low impurities and obtain high purity cassiterite. The impurity content of the concentrate also depends on the mining area and the pre-treatment steps that have been carried out previously. Good concentrates have low levels of impurity (high-grade). In this study, we combined the mechanical-magnetical separation and acid leaching method to optimize the purification process of cassiterite from a low-grade cassiterite concentrate in terms of increasing levels of Sn element and the intensity of X-ray diffraction from the cassiterite phase.

2. Experimental Procedures
2.1 Materials
The HCl (37%) and the ammonium solution 25% were purchased from MERCK with an analytical grade respectively. The high-pure water was used for preparation of all solution. In this study natural cassiterite concentrate were obtained from the mine site in the Delas area, Bangka Island.

2.2 Methods
The natural cassiterite concentrate is rinsed using water to eliminate all other related impurities such as soil and organic compound after that it dried in an oven. The purification process consists of two steps: mechanical-magnetical separation and acid leaching. The mechanical-magnetical separation step started by color separation (bright sand removal) and removed the magnetic elements of the concentrate subsequently. Dark sand which not attracted by the magnet was grounded to pass through a sieve 100 mesh before the acid leaching. The leaching step was performed using hydrochloric acid 30% with a solid to solvent ratio of 1:10 stirred at 70ºC for 1 hour. The subsequent leaching filtrate precipitated using ammonium solution at different pH 5, 7, and 9 then heated at 800ºC for 3 hours in the furnace.

2.3 Characterization of sample
The chemical element composition and the phase composition of sample spectra characterized used XRF and XRD respectively.

3. Results and Discussion
The chemical element composition of the natural cassiterite concentrate from the mine site in the Delas area, Bangka Island are presented in Table 1.

Table 1. The chemical element composition of natural cassiterite concentrate from Delas, Bangka Island

Element	Content (% Wt)	Element	Content (% Wt)
Sn	31.60	Fe	10.28
Ti	20.57	Al	2.38
Zr	19.37	Y	1,34
Si	10.43	Others	4.03

The content of Sn element in the natural cassiterite concentrate wa 31.60% with the dominant impurity element including: 20.57% Ti, 19.37% Zr, 10.43% Si and 10.28% Fe. The phase analysis of

the diffraction data on the cassiterite concentrate is presented in Figure 1. The element Sn in the concentrate is confirmed as the cassiterite phase (SnO_2) as the dominant phase with high intensity relative to the other phases. While the impurities of Zr and Si in the form of zircon phase ($ZrSiO_4$), Si in the form of quartz phase, Fe and Ti in the form of ilmenite phase ($FeTiO_3$) and Fe in the form of hematite phase (Fe_2O_3). The monazite phase ($LaPO_4$) is confirmed with a small peak with the main element is La.

The purification method for concentrate depends on the identification of the chemical elements and phases composition of the concentrate. Zircon, quartz and monazite are non-magnetic minerals commonly found as impurity phases in cassiterite concentrates. Zircon and quartz are one of the main impurities of the cassiterite concentrate on Bangka Island. This mineral has a contrasting color with cassiterite. The color of zircon generally has a yellow to brown and the quartz has white to cream [10,11]. Whereas the color of monasite generally has a reddish-brown and found in the form of sand following the cassiterite concentrate and its attracted by magnets [11].
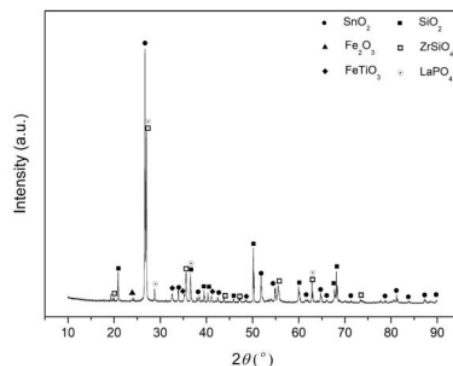

**Figure 1.** The XRD pattern of cassiterite concentrate

The separation process of the three phase impurities is carried out using the mechanichal separation method. The estwing pan use to separate concentrate based on density each mineral (phase). This method effective to reduce the wight and slight mineral. Density of each phase it different with others because it closed related with kind of constituent of atoms and it structured. Density also quite related with the color of minerals. The different color of mineral (phase) indicates its different mineral inline their density so different. When the estwing pan is rotating slowly and stably it make the same mineral (phase) in this case are the color of mineral will separate each other and remove the bright sand (quartz and zircon). After that dark sand remove the magnetic element by magnetic separation methods. This is successes to reduce hematite minerals and some ilmenite. Hematite and ilmenite have similar color with cassiterite but cassiterite are not atrracted magnet well. Hematite and ilmenite have reddish color on the sand and can be attracted by magnets [11,12]. Sometimes ilmenite also has weak magnetic properties when the composition of Fe is very low. The magnetical separation method is used to separate cassiterite from hematite and ilmenite using neodymium magnets. This magnet is a permanent magnet that has very strong magnetic power. This is made the minerals which are both strong and weak magnets can be optimally separated from the concentrate.

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Table 2. The chemical composition of product from mechanical-magnetical separation

Element	Content (% Wt)	Element	Content (% Wt)
Sn	85.56	Fe	2.30
Si	5.13	Ti	2.29
Al	2.97	Others	1.75

Table 3. The chemical composition of impurities from mechanical-magnetical separation

Element	Content (% Wt)	Element	Content (% Wt)
Sn	42.30	Mn	3.58
Fe	32.66	Al	2.18
Ti	9.18	Zr	1.71
Si	5.29	Others	3.10
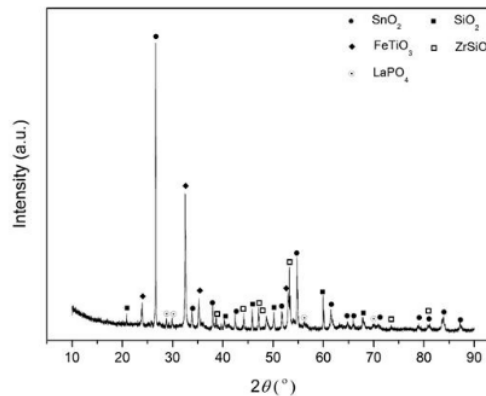
Figure 2. The XRD pattern of impurities from mechanical-magnetical separation

The chemical composition of the product by mechanical and magnetic separation is shown in Table 2. The element Sn increases significantly to 85.56% Wt from 31.60% Wt. This is testified by the analysis of diffraction data in Figure 3(b) revealed that the dominance of high-intensity cassiterite peaks. Zr content in zircon minerals decreased significantly followed by ilmenite, quartz and monazite. This is confirmed by the chemical content of the impurity of mechanical-magnetical separation in which the Zr, Ti, Fe and Si elements increase. However, there is still a high Sn content of 42.30% which is confirmed also from the peak of XRD pattern in Figure 2. It might caused by the manually operating of estwing pan so that when separating the impurity, cassiterite still taken.

Table 4. The chemical element composition of residue from acid leaching treatment

Element	Content (% wt)	Element	Content (% wt)
Sn	90.28	Ti	0.63
Fe	6.82	Al	0.21
Si	1.37	Others	0.69

The yield content of Sn from acid leaching treatment was reached up tu 90.28% wt increased relatively than yield after mechanical-magnetical steps. It caused by the solubility of the concentrate is quite low are 4.4%. There were no significant phase changes during acid leaching treatment as shown in Figure 3 (b) & (c).
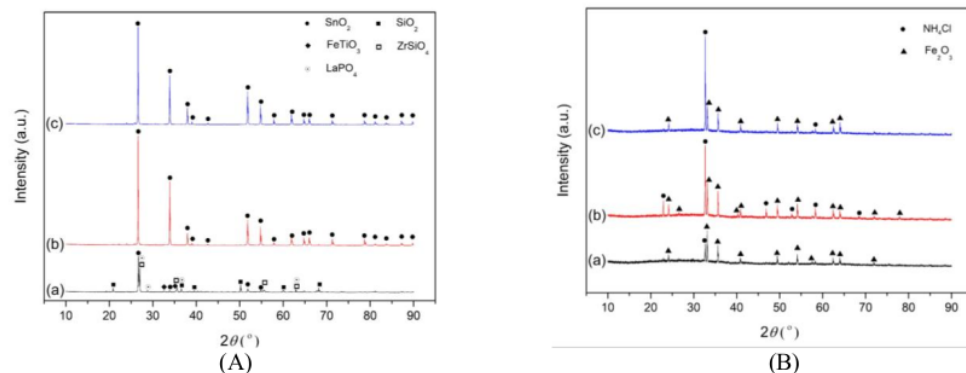
(A)   (B)

Figure 3. The XRD pattern of (A) cassiterite concentrate where (a) natural cassiterite concentrate, (b) product from mechanical-magnetical separation, & (c) residue from acid leaching treatment and (B) the filtrate crystalline compound at pH (a) 5, (b) 7, & (c) 9

The compound in the acid leaching treatment filtrate consists of cassiterite, hematite and ammonium chloride. The phase composition varies with variations in the pH of the precipitation. At the acid condition (pH 3) the hematite phase is greater than ammonium chloride. This is because the ammount of Fe^{3+} ions are abundant and it attracted more to bind OH^- ions than NH^{4+} ions. At pH 7 the amount of NH^{4+} ions are slightly higher than Fe^{3+} ions so that the ammonium chloride phase composition is slightly higher than hematite.

Table 5. The phase composition of filtrate crystalline compound

pH	Cassiterite (%)	Hematite (%)	Ammonium Chloride (%)	Rxp
5	4.2	71.7	24.0	9.05
7	4.7	42.3	53.0	9.16
9	0.9	4.6	94.5	9.58

The cassiterite phase is formed in small amounts, this indicates that there is a soluble cassiterite during the leaching process, although it is not quite significant. In the leaching process the element Fe (hematite) dissolves in HCl however Zr and Si elements in zircon and Ti in ilmenite are stable state and dissolve slightly. The metal oxides formed at acidic pH because the amount of metal dissolved in the filtrate is relatively low so that excessive of ammonium solution will actually cause the formation of chloride salts.

4. Conclusion

Cassiterite concentrate from the Delas mine area, Bangka Island has a composition of the dominant element Sn of 31.60% Wt as cassiterite phase and the phase of impurities such as zircon, hematite, ilmenite, quartz and monazite. The composition of Sn element increased significantly by 90.28% Wt after going through the mechanical-magnetical separation step followed by acid leaching using HCl solution. The solubility of cassiterite concentrate in the acid leaching process is very low at 4.4%, this indicates that the Sn element is difficult to decompose under these conditions. Consequently, the study successfully indicated that using mechanical-magnetical separation and acid leaching on the purification process could realize the cassiterite impurity removal and provide significantly increment of cassiterite purity from low-grade cassiterite concentrate.

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