The effect of pretreatments on the dissolutions of impurities from Indonesian cassiterite mineral

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Abstract. The purpose of this research was to purify cassiterite from associated minerals (impurities) and to investigate the effects of pretreatment on the dissolution of impurities from Indonesian cassiterite mineral. The steps of this research are as follows: characterization, pretreatment and leaching processes by dilute hydrochloric acid (HCl) solution. Firstly, cassiterite was characterized by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) techniques, and then pretreatment was carried out including washing, roasting at 700°C and both combinations of washing and roasting at 700°C. Cassiterite obtained from the processes of pretreatment and without pretreatment was then leached using 10% HCl solution with temperature variations of 35°C–150°C for 2 hours in atmospheric condition. The results showed that the chemistry composition of cassiterite was as follows: 57.82% Sn, 0.45% Si, 1.45% Ti, 1.79% Fe, 3.43% La, 3.37% Ce and 31.69% others. The best condition for purification of cassiterite was leaching without pretreatment that has the highest dissolution of associated mineral from cassiterite than other processes (pretreatment) for leaching at 110°C for 2 hours. This research was able to purify cassiterite with a chemical composition as follows: 66.14% Sn, 0.27% Si, 1.38% Ti, 1.18% Fe, 2.12% La, 2.03% Ce and 26.88% others. These results are quite satisfactory because this technology is quite simple and economical.

1. Introduction
One type of mineral that is widely available in Indonesia, particularly in Bangka Belitung island is cassiterite. Cassiterite or tin oxide which has the molecular formula (SnO$_2$) is the primary mineral producing tin and is quite abundant in the earth’s crust [1][2][3]. The cassiterite found in hard-rock deposits is associated with granitic host rock that needs further processes for separating associated minerals from SnO$_2$. Numerous techniques were developed such as classification, gravity concentration, and flotation techniques; however the minerals associated with such types of cassiterite deposits are harder to be separated because of its fine liberation size [3]. The hydrometallurgical processes were also applied to obtain SnO$_2$ high grade of cassiterite. Some researchers used a hydrometallurgical route as follows: Gerald et al. [4] tried to recover SnO$_2$ from cassiterite ore by microwave pretreatment, leaching and precipitation. Microwave treatment was selected due to the presence of associated minerals which behave differently and could be separated by microwave energy. The leaching processes conducted using -212 μm particle size of cassiterite, 1 – 8 M potassium hydroxide (KOH) solution and a temperature at 35°C, 55°C, 85°C and 103°C. The result showed the SnO$_2$ recovery by the microwave assisted process was 53%. It was higher than SnO$_2$ obtained by the untreated conventional method that was about 28%.
Baba et al. [5] reported that increase in the HCl concentration was accompanied with increase in the amount of cassiterite ore dissolved at various time. The rate of cassiterite ore dissolution is controlled by the hydrogen ion concentration \([H^+]\) that the reaction order is first order (for HCl concentration \(\leq 4 \text{ M}\)), with a correlation coefficient of 0.9995. The residual products consisted mainly of TiO\(_2\), FeTiO\(_3\), SiO\(_2\) and Ta\(_2\)O\(_5\) that was known as the unreacted materials by HCl solution. Yang et al. [6] has successful separated 99.4% iron from a low-grade tin concentrate by 150 g/L hydrochloric acid concentration at a temperature of 35\(^\circ\)C for 2 hours. The samples consisted of more than 50% cassiterite enwrapped by pyrite and limestone. It makes the iron components and other impurities could be dissolved by HCl solution. Lalasari et al. [7] in the previous research also tried to dissolve cassiterite-Indonesia by hydrochloric acid solution in various concentrations. The dissolution of cassiterite was not rising significantly with the increase of hydrochloric acid concentrations. Cassiterite in Indonesia contained mainly associated minerals such as quartz (SiO\(_2\)), ilmenite (FeTiO\(_3\)), xenotime and monazite that were difficult to be dissolved with HCl solution.

Cassiterite with high purity has now been developed into several functions which are as follows: nanomaterial SnO\(_2\) as gas sensors [8][9], SnO\(_2\)–TiO\(_2\) nanocomposites as adsorbent [10], antibacterial [11]. Cassiterite is also utilized as raw materials to make sodium stannate (\(\text{Na}_2\text{SnO}_3\)) which are widely used as electroplating, metal alloys of tin, and catalysts for organic synthesis [12]. Before cassiterite was utilized as raw materials for synthesizing tin chemical materials, it requires further processes for separating associated minerals from SnO\(_2\). In this study, we would investigate the effect of pretreatments prior to leaching on the dissolutions of impurities from Indonesian cassiterite mineral in variation temperatures. The leaching solvents used in the research was hydrochloric acid (HCl) that is a strong acid and more reactive than other acid solvents. The HCl solution is expected to separate associated minerals of cassiterite maximally.

2. Experimental

2.1. Material
Cassiterite was originally from Bangka Island in South Sumatra, Indonesia that has a chemical composition shown in table 1. The leaching reagent was purchased from Merck with an analytical grade of 37% hydrochloric acid (HCl).

| Element | Sn | O  | La  | Ce  | Nd | Fe | P  | Ti  | Ca  | Al  | Si  |
|---------|----|----|-----|-----|----|----|----|-----|-----|-----|-----|
| Percentage (%) wt | 57.82 | 23.39 | 3.43 | 3.37 | 2.18 | 1.79 | 1.68 | 1.45 | 0.63 | 0.52 | 0.45 |

2.2. Methods
The procedures were similar to the previous researches carried out by Lalasari et al. (2015) [7]. Firstly, cassiterite was grinded to -100 mesh of particle size and characterized by X-Ray Fluorescence (XRF) apparatus and X-Ray Diffraction (XRD). Secondly, samples was carried out pretreatment processes including washing, roasting at 700 \(^\circ\)C and both combinations of washing and roasting at 700 \(^\circ\)C. The samples after pretreatments were characterized by XRD analysis, respectively. In this step was also prepared a leaching reagent that 37% HCl was diluted with aquadest to make a solution of 10% HCl. The 10% HCl solution was reagent used in every leaching process. Thirdly, 10 gram of cassiterite (without pretreatment and with pretreatment) was leached in 100 ml solution of 10% HCl at variation temperatures of 35 - 150 \(^\circ\)C for 2 hours in atmospheric conditions. The products were then filtered to separate filtrate and residue of cassiterite. Finally, filtrate was characterized by Induced Coupled Plasma (ICP) analysis and residue was characterized by XRF analysis.
3. Result and Discussion

According to Table 1 looked the chemical composition of cassiterite was follows as: 57.82% Sn, 23.39% O, 3.43% La, 3.37% Ce, 2.18% Nd, 1.79% Fe, 1.68% P, 1.45% Ti, 0.63% Ca, 0.52% Al, 0.45% Si and 2.67% others that was different with the cassiterite of previous researches by Lalasari (2015). The cassiterite used in this research has a lower tin percentage than previous samples (66.36% Sn). It probably due to the cassiterite that was not yet completely processed or pretreated furthermore such as comminution, classification, gravity concentration and magnetic separation. In this opportunity, we would explore the effect of pretreatment on the dissolution of impurities from Indonesian cassiterite mineral.

3.1. The effect of pretreatment on the formed phase

To study the pretreatments effects on the formed phase of cassiterite, samples prior to leaching with 10% HCl solution was applied some processes such as washing, roasting at 700 °C and both combinations of washing and roasting at 700 °C. The samples after pretreatments were characterized by XRD analysis that showed in figure 2.

Figure 2 shows that cassiterite with pretreatment such as roasting at 700 °C and both combinations of washing and roasting at 700 °C was more crystalline than cassiterite without pretreatment. The crystallinity of cassiterite increased after roasting at 700 °C. The phase of cassiterite has not changed that the peaks of diffraction was clearly and sharply at 2θ degree of 26.67°; 33.95°; 38.02°; 51.85°; 54.84°; 61.96°; 64.85°. The existence of peaks indicated that cassiterite for conditions such as without and with pretreatment has a diffraction pattern in accordance with ICSD No. 9163, namely stannum dioxide (SnO₂). The diffraction peaks of impurities still appeared shortly at 2θ degree of 28.89°; 31.21°; 39.05° as La₅Sb and 2θ degree of 29.87°; 42.67°; 61.96° as CeSe. The other impurities were not found such as Nd, Fe, Ti, Ca, Al, Si, P, etc because they have lower intensities of diffraction peaks.

The phase of cassiterite after pretreatment has not changed because the processes such as roasting at 700 °C and leaching with water has not caused formation of new phase of cassiterite. The washing process only dissolved organic compounds and associated minerals of cassiterite by gravity concentration and also cassiterite would keep stable although roasted at 700 °C. This pretreatment was almost suitable with experiment conducted Zhang et al [12]. He explained that cassiterite (SnO₂) seldom reacted with air during the roasting at 900 °C for 120 min.

3.2. The effect of pretreatment on the dissolved cassiterite

Based on the result of XRD analysis, pretreatment effects such as roasting and both combinations of washing and roasting have not changed the phase of cassiterite and only increasing crystallinitity of
cassiterite. The effect of crystallinity on the dissolution of cassiterite would be investigated in this experiment. The cassiterite samples resulted from pretreatment were leached with 10% HCl solution for 2 hours in various temperatures and pretreatments. The results are shown in Figure 3.

The dissolution of cassiterite rose gradually with the increase of leaching temperature at all conditions. The highest dissolution was showed on samples without pretreatment that the dissolved cassiterite was approximately 4.1%. This result was enough interesting and could become a basic to purify cassiterite which was simple and economical. Cassiterite without pretreatment was easier dissolved than cassiterite with pretreatment. The increase of crystallinity would make cassiterite was difficult to be dissolved by 10% HCl solution. Cassiterite and other associated minerals become more stable after roasted. According to Figure 3, the grade of cassiterite dissolution prior to be leached by 10% HCl solution was cassiterite without pretreatment, cassiterite with washing pretreatment, cassiterite with roasting pretreatment at 700°C and cassiterite with both pretreatment combinations of washing and roasting at 700°C.

![Figure 3. The dissolved cassiterite in variation conditions](image)

Figure 3 also shows that the dissolution of cassiterite by 10% HCl solution was insignificant compared to experiment carried out by Yang et al (2014) [6]. Yang et al [6] has successful separated 99.4% iron from a low-grade tin concentrate by 150 g/L hydrochloric acid concentration at a temperature of 35°C for 2 hours. The cassiterite samples used by Yang et al were originally from China that consisted of more than 50% enwrapped by pyrite (FeS) and limestone. They were more soluble in HCl solution. The characteristic of cassiterite from China was different with cassiterite from Indonesia. Cassiterite from Bangka Island, Indonesia consisted of associated minerals such as quartz, ilmenite, rutile, xenotime and monazite that were harder to be dissolved by HCl solution [7]. The dissolution of associated minerals was proportional to the percentage of dissolved cassiterite by HCl solution. The low percentage of dissolved cassiterite by HCl solution showed the less percentage of associated mineral separated from cassiterite.

3.3. The effect of pretreatments on the dissolution of Fe, Ti, Si and Sn elements

To explore the dissolution of impurities from cassiterite by dilute HCl solution, filtrate from the dissolved cassiterite was analyzed by ICP-OES. The elements of filtrate measured in this experiment were few such as iron (Fe), titanium (Ti), silica (Si) and tin (Sn). The results are shown in figure 4.

Figure 4 describes the dissolution of Fe, Si, Ti, and Sn elements by dilution in HCl solution. As shown in figure 4, the increase of leaching temperature was accompanied with the rise in the amount of dissolved elements from cassiterite. However, the dissolution of Fe, Si, Ti and Sn elements was insignificant in all conditions. It was found the dissolution of Fe element higher than Ti, Si and Sn elements that was about 47.92% for leaching cassiterite without pretreatment. The dissolution of Fe element was still less than the experiment carried by Yang et al [6] that could separate 99.4% iron from a low-grade tin concentrate (cassiterite) by HCl solution. These were probably caused by the fact
that cassiterite in Indonesia consists of FeTiO$_3$ mineral and was more dominant than FeO and FeS$_2$ minerals. Therefore, the Fe element of cassiterite was difficult to be dissolved in HCl solution.

Figure 4 also shows that the dissolution of Si and Ti elements were low enough at all conditions. The highest dissolution of Si and Ti elements were approximately 17.87% and 0.49%, respectively. The Si associated mineral of cassiterite was indicated as quartz (SiO$_2$), whereas the Ti associated mineral was predicted as ilmenite (FeTiO$_3$) and rutil (TiO$_2$). These minerals have a slightly higher solubility in HCl solution. Baba et al. [5] also explained the residual products of cassiterite from Nigeria consisted mainly of TiO$_2$, FeTiO$_3$, SiO$_2$ and Ta$_2$O$_5$ that was known as the unreacted materials by HCl solution. In this experiment, it was looked that the Sn element was almost insoluble in HCl solution that was only about 0.06%. These was really expected to purify cassiterite from associated minerals.

**Figure 4.** The dissolution of Fe, Si, Ti and Sn in variation pretreatments and temperatures

3.4. *The effect of pretreatment on the chemistry composition of cassiterite residue*

To know the chemical composition of cassiterite leached by dilute HCl solution, residue of cassiterite was characterized by XRF analysis. The result is shown in table 2.

**Table 2.** The chemical composition of cassiterite residue

| Element | Sn  | O    | La   | Ce   | Nd   | Fe   | P    | Ti   | Ca   | Al   | Si   |
|---------|-----|------|------|------|------|------|------|------|------|------|------|
| A (%wt) | 57.82 | 23.39 | 3.43 | 3.37 | 2.18 | 1.79 | 1.68 | 1.45 | 0.63 | 0.52 | 0.45 |
| B (%wt) | 66.14 | 22.50 | 2.12 | 2.03 | 0.96 | 1.18 | 1.00 | 1.38 | 0.00 | 0.00 | 0.27 |
| C (%wt) | 59.98 | 22.58 | 3.15 | 3.20 | 2.07 | 1.56 | 1.24 | 1.40 | 0.00 | 0.00 | 0.25 |

Note: A is cassiterite samples; B is cassiterite residue without pretreatment; C is cassiterite residue with pretreatment (roasting at 700 °C)
As shown in table 2 that cassiterite without pretreatment has a purity higher compared to cassiterite with pretreatment (roasting at 700 °C). The purification of cassiterite reached in this experiment was about 66.14% Sn from 57.82% Sn (cassiterite samples). The roasting pretreatment to cassiterite only increased crystallinity and caused associated minerals of cassiterite become more stable so that it was more difficult to be dissolved in HCl solution. The result was similar to the experiment by Zhang et al [12]. He tried to upgrade cassiterite using roasting at 900 °C for 120 min and leaching with 25% HCl solution. It was found that that cassiterite was insoluble in hydrochloric acid. The purity of cassiterite only increased about 62.93% Sn from 42.92% Sn.

4. Conclusion
The chemistry composition of cassiterite from Bangka in Indonesia is as follows: 57.82% Sn, 0.45% Si, 1.45% Ti, 1.79% Fe, 3.43% La, 3.37% Ce and 31.69% others. The phase of cassiterite has not changed after carried out by pretreatment (washing; roasting and both combinations of washing and roasting. Cassiterite from Bangka in Indonesia consisted of quartz, ilmenite, rutile, xenotime and monazite mineral that were difficult dissolved by HCl solution. The best condition for purification of cassiterite was process of leaching without pretreatment that has the highest dissolution of associated mineral than other processes. This research was able to purify cassiterite with a chemical composition as follows: 66.14% Sn, 0.27% Si, 1.38% Ti, 1.18% Fe, 2.12% La, 2.03% Ce and 26.88% others.

Acknowledgments
The authors are grateful for the main financial supports from the thematic program of Research Center for Metallurgy and Material, Indonesian Institute of Science (LIPI) and thanks for contributing from Dea Sidawayat Bharani, Bogor Agricultural University (IPB) in this experiment.

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