Preliminary Study on the Dissolutions of Ce, Nd, Y and La from Mineral Cassiterite by Acid and Alkaline Leaching

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Abstract. Rare Earth Metal is a rare element that its availability in nature is very small. In Indonesia, the potential of rare earth metals is generally found as the associated mineral in major commodities, especially gold and alluvial tin. These associated minerals can be processed using a particular technology so that the result is a by-product that can increase the added value of the mineral. The purpose of this research was to investigate the dissolution of Cerium (Ce), Neodymium (Nd), Yttrium (Y) and Lanthanum (La) from mineral cassiterite by leaching process using dilute hydrochloric acid (HCl), sulfate acid (H₂SO₄) and sodium hydroxide (NaOH). Firstly, cassiterite was grinded to -100 mesh of particle size and characterized by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) techniques. Secondly, 10 gram of cassiterite was leached in 100 ml solution of 3.26 N HCl, H₂SO₄ and NaOH at variation leaching time of 2, 4, 6, 24 and 48 hours in atmospheric conditions. The products were then filtered to separate filtrate and residue of cassiterite. Finally, to investigate the dissolution of Ce, La, Nd and Y, filtrate from dissolved cassiterite was analyzed by Induced Coupled Plasma-Optical Emission Spectrometry (ICP-OES), while to know the chemical composition of cassiterite leached by dilute HCl, H₂SO₄ and NaOH, residue products of cassiterite was characterized by XRF analysis. The result of ICP-OES analysis showed the dissolution of Ce element higher than Nd, Y and La elements for leaching cassiterite using HCl, H₂SO₄ and NaOH. The increase of leaching time was accompanied by the rise in the amount of dissolved elements from cassiterite. The result of XRF analysis showed the chemistry composition of Ce, Nd, Y and La elements on residue decreased insignificantly from chemistry composition of cassiterite (raw mineral) in all conditions. However, the dissolution of Ce, La, Nd and Y was insignificant in all conditions.

1. Introduction
Indonesia is one of the countries rich in mineral resources. Several studies have shown that some minerals contain undeveloped rare earth metals. Rare Earth Metal is a rare element that its availability in nature is very small. The use of rare earth metals is very broad and closely related to high-tech products such as computer, telecommunication, nuclear and aerospace industries. In the future it is estimated that the use of rare earth metals is increasingly proportional to the development of such high technology. Rare earth metal is the trigger for the birth of new technologies that will continue to grow such as LCDs, magnets and hybrid batteries. This resulted in demand for rare earth metals will

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continue to increase. Its incapacity in nature is rare and the level of use for high technology is increasingly widespread, resulting in the price tends to increase.

In Indonesia, the potential of rare earth metals is generally found as the associated mineral in major commodities, especially gold and alluvial tin. These associated minerals can be processed using a particular technology so that the result is a by-product that can increase the added value of the mineral. The potential of gold and tin precipitation as a carrier of rare earth metals is rarely spread across several islands in Indonesia. It is found as the associated mineral of main mineral. The tin ore contains the main minerals of cassiterite (SnO₂) and associated minerals such as columbit-tantalite [(Fe, Mn) (Ta,Nb)₂O₆], zircon (ZrSiO₄), ilmenite (FeTiO₃), rutile (TiO₂), quartz (SiO₂), pyrite (FeS₂), xenotime (YPO₄) and monazite (Ce, La, Y, Th) PO₄. The results of Lalasari et al's study [1] explain that the cassiterite minerals from Bangka, Sumatera, Indonesia contain 3.43% Cerium (Ce), 3.47% Lanthanum (La), 2.18% Neodymium (Nd) and 0.36% yttrium (Y).

Many researchers had reported the result of their investigation, such as: F. Habashi succeeded in extracting of rare earth elements from monazite and xenotime by leaching process with sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄)[2]. Kim et. al used the sulfuric acid leaching after mechanochemical treatment of beneficiated monazite (212 µm size) obtained from the beach sand deposit of Malaysia with sodium hydroxide at room temperature[3]. Kuzmin et. al has reported the nitric acid to leach out the metals from the ground RE ore of Chuktokon deposits, Russia containing 3–7% REOs in the phosphate form (monazite, turnerite, florensite), Fe–Mn oxides and 0.5–1% Nb oxide (chalcolamprite) in a rotating autoclaves. REEs recovery of 87–90% is obtained during leaching in autoclave in the temperature range of 180–220 °C of the ground ore [4]. Kumari and co-worker studied two step leaching of Korean monazite using diluted HCl at moderate temperature for 2 h and pulp density < 100 g/L resulting in only 25% REMs dissolution [5]. Then the concentrate left after phosphate removal was leached in 6 N HCl at 90 °C for 2 h maintaining 60 g/L pulp density resulting in 90% REMs recovery [6].

Various methods have been undertaken to increase the levels of rare earth metals in the main minerals. These include, for example, multilevel precipitation, multilevel crystallisation, ion exchange columns and liquid extraction by attempting various solvents which are selective to one of the desired elements. Separation by way of extraction is mostly done because it has many advantages when compared with other ways that is in terms of process, time and more simple equipment [7]. The purpose of this experiment is to study the solubility of rare earth (Ce, Nd, Y and La) elements in the cassiterite ore in acidic and basic solutions. The acid and base solutions used in this experiment are sulfuric acid (H₂SO₄), hydrochloric acid (HCl) and sodium hydroxide solution (NaOH).

2. Experimental
The raw material used in the experiment was cassiterite ore obtained from Bangka Island, Indonesia. The chemical composition of cassiterite minerals used can be seen in Table 1.

| Table 1. The chemical composition of cassiterite from Bangka Island, Indonesia |
|-------------------|-------|------|-----|----|-----|----|-----|-----|-----|-----|
| Element | Sn | La | Ce | Nd | Fe | P | Ti | Ca | W | Al | Y |
| % Wt | 57.82 | 3.43 | 3.37 | 2.18 | 1.79 | 1.68 | 1.45 | 0.63 | 0.62 | 0.52 | 0.36 |

This experiment has four stages of activities that are sample preparation, leaching process, filtration and characterization. In the sample preparation, the cassiterite minerals were grinded to a size of -100 mesh using a disc mill, then characterized by XRF to know the chemical composition as shown in Table 1.

In the leaching process, 10 grams of cassiterite were weighed, then dissolved in the three neck flask using variation solvents: 100 ml of HCl 3.26 N, 100 ml of H₂SO₄ 3.26 N and NaOH 3.26 N obtained from dilution. The dissolution process was done with variation times of 2, 4, 6, 24, and 48
hours at temperature 100 °C-110 °C. For NaOH solvent, leaching process was done without using condenser, with variation times of 2, 4, and 6 hours.

The result of the leaching process is filtered by whatman paper No. 42, and obtained filtrate and residue. The residue is then washed with distilled water until the pH approaches 7 and continued the drying process in the oven at 110 °C for one hour. After one hour, the filter paper containing the residue was weighed in cold conditions and calculated for weight reduction of each experimental variable. The last step was characterization that filtrate product was analyzed using ICP-OES and residue product characterized by XRF.

The reaction of Rare earths elements (Ce, La, Y, Th) PO₄ with H₂SO₄ and NaOH could be described as follows [8]:

\[
2 \text{REPO}_4^- + 3 \text{H}_2\text{SO}_4 \rightarrow \text{RE}_2(\text{SO}_4)_3 + 6\text{H}^+ + 2\text{PO}_4^{3-} \quad (1)
\]

\[
\text{REPO}_4^- + 3 \text{NaOH} \rightarrow \text{RE(OH)}_3 + \text{Na}_3\text{PO}_4 \quad (2)
\]

while the reaction of Rare earths elements (RE)OH with HCl could be described as follows:

\[
\text{RE(OH)}_3 + 3 \text{HCl} \rightarrow \text{RECl}_3 + 3\text{H}_2\text{O} \quad (3)
\]

3. Results and discussion

To investigate the solubility of Ce, La, Nd and Y from cassiterite in variation solvents, it is necessary to observe visually and characterize the product from the leaching process using ICP-OES analysis to identify the solubility of Ce, La, Nd, Y from the filtrate and XRF analysis for know the chemical composition of the residue. The experimental results and characterization are discussed below.

3.1. The Filtrate Color of Leaching Process

![Figure 1](image1.png)

**Figure 1.** The filtrate of leaching process in variation solvent:
(a) H₂SO₄; (b) HCl; (c) NaOH

Figure 1 represented the color of filtrate in the various solvent of leaching process. Fig. 1a, the color of the filtrate of leaching process with H₂SO₄ solution was not changed significantly while Fig.1b, the
filtrate changed to be the dark green color with increasing the time of leaching process (2-48 hours) of HCl solution. The change of filtrate color indicated that cassiterite dissolved a lot shown in Fig. 2.

Fig. 1c represented the color of filtrate to be the dark orange color with increasing leaching time (2-6 hours) of NaOH solution. The change of filtrate color indicated that cassiterite dissolved significantly in NaOH solution. The same is done on previous research that F. Habashi [2] where succeeded in extracting of rare earths elements by leaching process with sodium hydroxide (NaOH).

3.2. The Dissolution of Cassiterite

![Figure 2. The percentage of dissolved cassiterite in variation solvent (HCl, H_2SO_4, NaOH)](image)

Fig. 2. showed the percentage of dissolved cassiterite in various concentrations. The percentage of dissolved cassiterite rise in proportion to the increase of leaching time. The percentage of dissolved cassiterite was maximum at leaching time 4 hours with NaOH solvent that was about 9% and the dissolution of cassiterite was not rising significant with hydrochloric and sulfate acid. The same is done on previous research that Lalasari[1] where the dissolution of cassiterite was not rising significant with the increase of hydrochloric acid concentrations.

From the result of a investigation in Fig. 2 could be concluded that the dissolution of cassiterite was not rising significantly with the increase of leaching time in all condition of solvents.

3.3. The Dissolution of Ce, Nd, Y and La from Cassiterite

To study effects of leaching time on the dissolution of rare earth (Ce, Nd, Y, La) elements from cassiterite-Indonesia, 10 gr of cassiterite was dissolved in various solvents (HCl, H_2SO_4, NaOH) with variation of leaching time (2, 4, 6, 24, 48 hours) at temperature of 100-110°C. Mixture then was filtrated and filtrate was characterized by ICP-OES analysis. The result of filtrate and residue product were shown in Figure 3 and Table 2.
Figure 3. The concentration of dissolved rare earth elements in variation solvent HCl, H$_2$SO$_4$ and NaOH (ppm): (a) Ce; (b) Nd; (c) Y and (d) La

Figure 3 represented the result of ICP-OES analysis for concentration of dissolved rare earth (Ce,Nd,Y,La) elements. Fig 3 showed the dissolution of Ce element higher than Nd, Y and La elements for leaching cassiterite using HCl and H$_2$SO$_4$ solvents. The elements of cerium extracted higher than elements of Nd, Y and La. This condition described that Nd, Y and La was more stable than cerium in acid solution. The increase of leaching time was accompanied by the rise in the amount of dissolved rare earth elements from cassiterite. However, the dissolution of Ce, Nd, Y and La elements was insignificantly in all conditions.

Based on Fig 3, leaching cassiterite using H$_2$SO$_4$ solvent more difficult to dissolved than using HCl and NaOH solvent, because H$_2$SO$_4$ solvent more unstable than other processes. The same is done on previous research that Kumari[5] and Panda[6] where studied of rare earths elements from Korean monazite using diluted HCl at moderate temperature for 2 h and then the concentrate left after phosphate removal was leached in 6 N HCl at 90 °C for 2 h maintaining 60 g/L pulp density resulting in 90% REMs recovery.
3.4. The Chemical Composition of Residue Product from Leaching Process

Table 2. The chemical composition of residue product in variation solvents

| Element | HCl 2 hours | H2SO4 2 hours | NaOH 2 hours | HCl 48 hours |
|---------|-------------|---------------|--------------|--------------|
| Sn      | 64.85%      | 64.70%        | 64.61%       | 68.32%       |
| Ce      | 2.19%       | 2.20%         | 2.46%        | 1.42%        |
| La      | 2.33%       | 2.49%         | 2.67%        | 1.28%        |
| Si      | 0.24%       | 0.22%         | 0.11%        | 1.09%        |
| Ti      | 1.43%       | 1.36%         | 1.33%        | 0.88%        |
| Fe      | 1.29%       | 1.27%         | 1.46%        | 0.76%        |
| P       | 1.00%       | 1.01%         | 1.08%        | 0.70%        |
| Nd      | 1.12%       | 1.38%         | 1.33%        | 0.68%        |
| Cl      | 0.38%       | 0.39%         | 0.41%        | 0.36%        |
| W       | 0.37%       | 0.48%         | 0.19%        | 0.30%        |
| Zr      | 0.30%       | 0.30%         | 0.29%        | 0.27%        |
| Y       | 0.26%       | 0.29%         | 0.28%        | 0.26%        |
| Pr      | 0.37%       | 0.44%         | 0.45%        | 0.21%        |
| Cd      | 0.20%       | 0.16%         | 0.08%        | 0.18%        |
| Sb      | 0.12%       | 0.08%         | 0.11%        | 0.11%        |
| Cr      | 0.13%       | 0.13%         | 0.12%        | 0.09%        |
| Ta      | 0.07%       | 0.10%         | 0.09%        | 0.08%        |
| Nb      | 0.07%       | 0.07%         | 0.07%        | 0.07%        |
| V       | 0.07%       | 0.07%         | 0.06%        | 0.07%        |
| Te      | 0.09%       | 0.04%         | 0.11%        | 0.06%        |
| S       | 0.08%       | 0.09%         | 0.09%        | 0.04%        |
| Pb      | 0.02%       | 0.03%         | 0.03%        | 0.02%        |

Table 2 describes the result of XRF analysis from residue products that showed the chemistry composition of rare earth (Ce, Nd, Y and La) elements on residue product decreased insignificantly than the chemistry composition of cassiterite (raw mineral) in all conditions. The small change of the chemistry composition indicated that rare earth (Ce, Nd, Y and La) elements dissolved insignificantly in HCl, H2SO4 and NaOH solvents.

4. Conclusion

The result of ICP-OES analysis showed the dissolution of Ce element higher than Nd, Y and La elements for leaching cassiterite using HCl, H2SO4 and NaOH. The increase of leaching time was accompanied by the rise in the amount of dissolved rare earth elements from cassiterite. Leaching cassiterite using H2SO4 more difficult to dissolve than using NaOH and HCl. The result of XRF analysis showed the chemistry composition of Ce, L, Nd and Y elements on residue products decreased insignificantly from chemistry composition of cassiterite (raw mineral) in all conditions.
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