An Efficient Extraction and Selective of Alumina from Lapindo Mud

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Abstract. Lapindo mud, a soft clay soil found in Sidoarjo, East Java, has a high water and mineral content. It contains 16% alumina (Al_2O_3), making it a potential source of aluminum metal. The high content of silica oxide in Lapindo mud is of particular interest to separate the oxide from the alumina oxide. Silica oxide is insoluble in acid while aluminum oxide is soluble in acid. The alumina extraction process was carried out using acid solvent. The dried mud with a size of ≤100 mesh was extracted using HNO_3 and HCl solvent with concentration of 4, 6, and 8 M at temperatures of 60°C, 70°C, and 80°C for 100, 200, and 300 minutes. The extraction results were filtered, then the pH of the filtrate was adjusted to 12 with 6 M NaOH. The filtrate was filtered, thus Fe^{3+} was obtained as a residue. The filtrate was neutralized to pH 8 using 6 M HCl. The filtrate was filtered to obtain $NaAlO_2$. The precipitate formed was washed using distilled water and dried in an oven to obtain $Al(OH)_3$. $Al(OH)_3$ was then calcined at 600°C for four hours to form Al_2O_3. The results showed that acid solvent concentration, extraction temperature, and heating time affected the mass of Al_2O_3 obtained. Increasing acid solvent concentration, extraction temperature, and heating time, increases the mass of Al_2O_3 obtained. The mass of Al_2O_3 obtained was 1.19 grams for HNO_3 solvent and 1.63 grams for HCl solvent with concentration of 8 M, extraction temperature of 80°C, and heating time of 300 minutes. The results of XRF characterization show that the Al_2O_3 purity level is 42.8% and 27.3%with HNO_3 and HCl solvent, respectively.

1 Introduction

The Sidoarjo Mud Flow, known as LUSI (Lumpur Sidoarjo), is the result of a mud eruption at the drilling site of PT Lapindo Brantas in Renokenongo Village, Porong, Sidoarjo, East Java. This mud eruption stemmed from a borehole leak during the oil and gas exploration activities. The local community, particularly in Porong, has experienced various health, environmental, and economic losses due to this ongoing mud flow. Comprehensive knowledge of the characteristics of the Sidoarjo mud flow is crucial for its utilization and management.

The Lapindo mud reported that the Lapindo mud contains oxide compounds such as aluminum oxide, silicon dioxide, potassium oxide, titanium oxide, calcium oxide, manganese

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oxide, phosphorus pentoxide, sulfur oxide, vanadium pentoxide, and others [1]. in a different study similar findings regarding the mineral composition contained in the Lapindo mud [2]. All research results regarding the composition indicate that silicon dioxide is the dominant mineral in the Lapindo mud, followed by iron oxide and aluminum oxide. The high content of aluminum oxide (approximately 18.27%) in the Lapindo mud can be utilized as a supporting material for metal catalysts by separating this oxide from silica oxide [3]. The insoluble nature of silica oxide in acid can be utilized to obtain pure alumina oxide.

Aluminum oxide is a chemical compound with the chemical formula Al_2O_3. The mineral name of aluminum oxide is alumina. Aluminum oxide is a good heat and electrical insulator, so it is widely used as an abrasive material for components in cutting tools. In addition, it is widely used in the field of mechanical engineering to manufacture machine parts that are resistant to fire and high temperatures. The medical field also uses it as a material for making dental implants. This is due to its properties of high strength, hardness, wear resistance, refractory resistance, thermal conductivity, chemical resistance and electrical strength [4]. Generally, alumina is found in a crystalline form called corundum or α-aluminum oxide.

Aluminum oxide or alumina can be obtained through an extraction process. Extraction is a separation process that is based on the difference in solubility between two liquids. There are many methods that can be used to carry out the extraction process, including: maceration, soxhlet, reflux and percolation. Alumina itself can be obtained through the reflux extraction method. The reflux extraction method is a solid-liquid extraction process at a constant temperature. Reflux extraction is carried out by repeatedly evaporating the solvent and continuing with condensation for a certain period of time without any loss of solvent [5]. The principle of the reflux extraction method is that the solvent used will evaporate at a high temperature, then be cooled with a condenser so that the solvent which was initially in the form of vapor will condense in the condenser. There is a phase change to liquid and the solvent falls back into the reaction container so that it will remain there throughout the reaction [6]. This method is suitable for use on materials that are resistant to heating.

Several studies have been conducted to obtain alumina from various sources, including Lapindo mud. From the previous research extracted Lapindo mud with HCl solvent with various types of concentrations (1, 2, 3, 4, 5, and 6 M) for 20 minutes with and without heating. The result shows that the highest yield was obtained in 6M HCl solvent with a yield value without heating of 18.59% and with heating of 62.45%. The alumina that has been obtained was then characterized by the SSA method [7].

2 Materials and Methods

2.1 Material

Lapindo mud used in this study was collected from Sidoarjo Regency, East Java, Indonesia. The chemicals used in this study were HNO3 with purity of 65%, HCl with purity of 32%, and sodium hydroxide.

2.2 Lapindo mud pretreatment

A schematic flow diagram of pretreatment process and extraction process of alumina from Lapindo mud shown in Figure 1

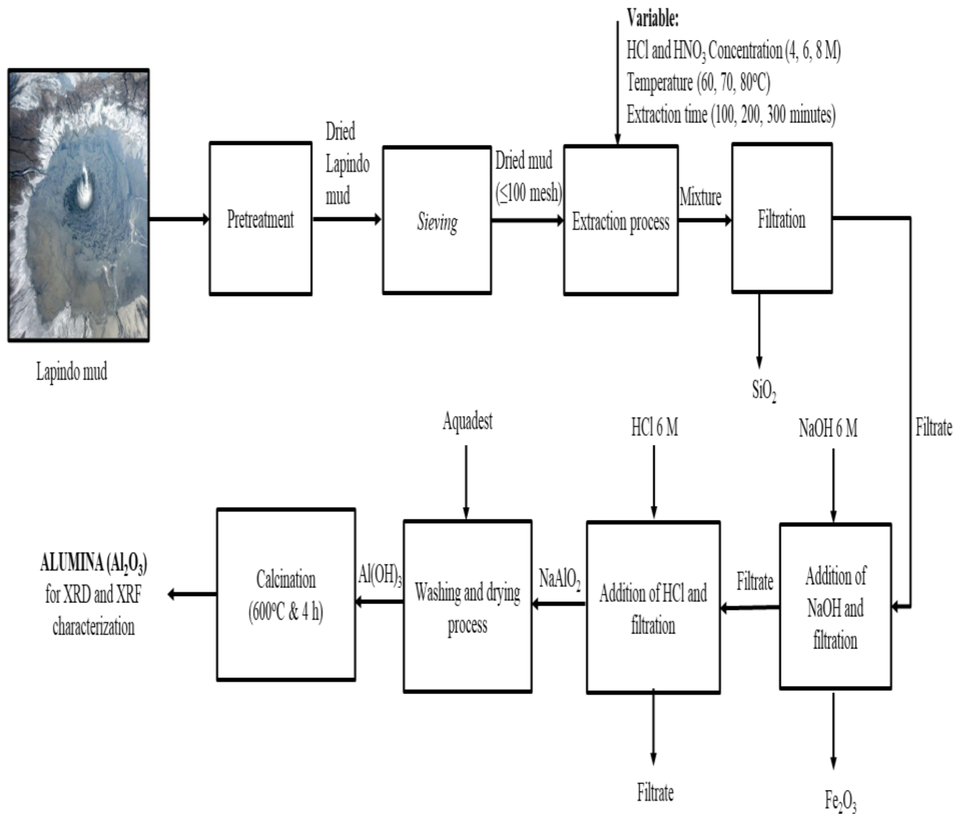

Fig. 1. Flow diagram of alumina extraction from Lapindo mud

The Lapindo mud was dried using an oven and then sieved to 100 mesh using hammer mill.

2.3 Extraction of alumina from Lapindo mud

The dried mud with a size of ≤100 mesh was extracted using HCl and HNO_3 solvent with concentration of 4 M, 6 M, and 8 M at temperatures of 60°C, 70°C, and 80°C for 100 minutes, 200 minutes, and 300 minutes. The mixture was filtered, then the pH of the filtrate was adjusted to 12 with 6 M NaOH. The mixture was then refluxed at 70°C for 200 minutes. The mixture was filtered, thus Fe^{3+} was obtained as a residue. The filtrate was neutralized to pH 8 using 6 M HCl, then the mixture was refluxed at 70°C for 200 minutes. The mixture was filtered to obtain $NaAlO_2$ as a residue. The precipitate formed was washed using distilled water and dried in an oven to obtain $Al(OH)_3$. $Al(OH)_3$ was then calcined at 600°C for four hours to form Al_2O_3. The purity of alumina was determined by X-ray Fluorescence and the crystallinity of alumina was determined by X-ray Diffraction.

3 Results and Discussion

Equations should be centred and should be numbered with the number on the right-hand side.

Table 1. Yield of alumina obtained

Variables	Alumina Yield using HNO_3 Solvent	Alumina Yield using HCl Solvent
4 M, 60°C, 100 minutes	2.31%	2.47%
4 M, 70°C, 100 minutes	2.63%	2.59%
4 M, 80°C, 100 minutes	3.01%	3.58%
6 M, 60°C, 200 minutes	3.3%	4.07%
6 M, 70°C, 200 minutes	6.44%	6.05%
6 M, 80°C, 200 minutes	7.63%	8.27%
8 M, 60°C, 300 minutes	7.84%	5.06%
8 M, 70°C, 300 minutes	15.77%	7.53%
8 M, 70°C, 300 minutes	20.06%	14.69%

3.1 Effect of Extraction Time on Alumina Yield

Time of the extraction process is one of the factors that will affect the alumina yield obtained. In this study, the extraction process was carried out with two types of acid, which is HCl and HNO_3 with extraction time for 100, 200, and 300 minutes. The results showed that the longer extraction time, the more alumina yield obtained. The result of alumina yield with time variables are shown in Figure 2 and Figure 3.

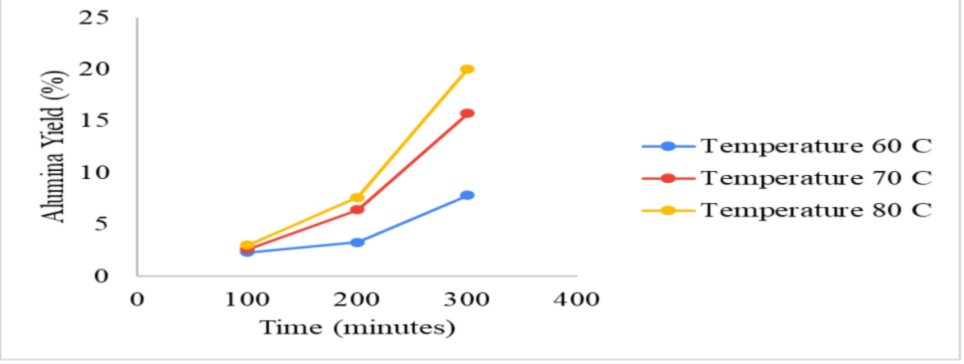

Fig. 2. Effect of extraction time on alumina yield for HCl solvent

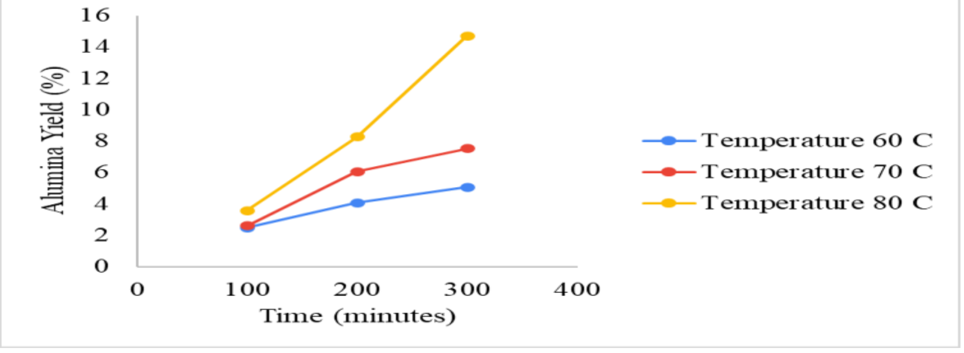

Fig. 3. Effect of extraction time on alumina yield for HNO_3 solvent

Based on Figure 2 and 3 above, the result indicates that the highest alumina yield was achieved at extraction time 300 minutes, for both HCl and HNO_3, which was 20.06% and 14.69%, respectively.

Previous research conducted [8], shows a directly proportional relationship. Where the longer the extraction time, the greater the alumina yield obtained. Another study conducted by [9] also showed that alumina recovery increased with increasing extraction time. At an extraction time of 15 minutes, the aluminum obtained reached 63.51%. Meanwhile, at an extraction time of 30 minutes, the aluminum obtained reached a maximum value of 87.89%. The extraction rate increases significantly at the beginning of time, then slows down and finally remains constant after reaching a certain time. This shows that the alumina obtained has reached its maximum amount.

In this study, the highest alumina yield was achieved at 300 minutes of extraction time for both HCl and HNO_3, with respective yields of 20.06% and 14.69%. This indicates that an increase in extraction time influences the extraction rates and alumina yield obtained.

3.2 Effect of Acid Concentration on Alumina Yield

Acid concentration plays a significant role in extracting alumina from Lapindo mud. In this study, the alumina extraction process was carried out using two types of acid, HCl and HNO_3, at concentrations of 4 M, 6 M, and 8 M. The results of alumina yield obtained with acid concentration variables are shown in Figure 4 and Figure 5.

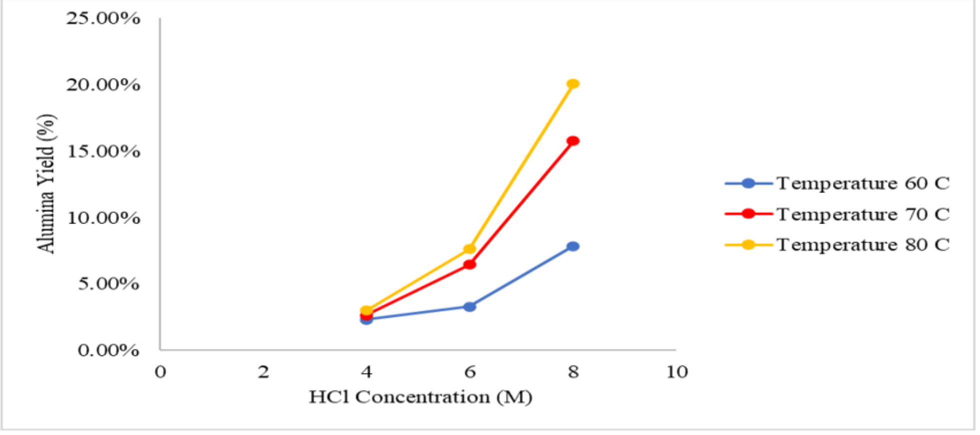

Fig. 4. Effect of HCl concentration on alumina yield

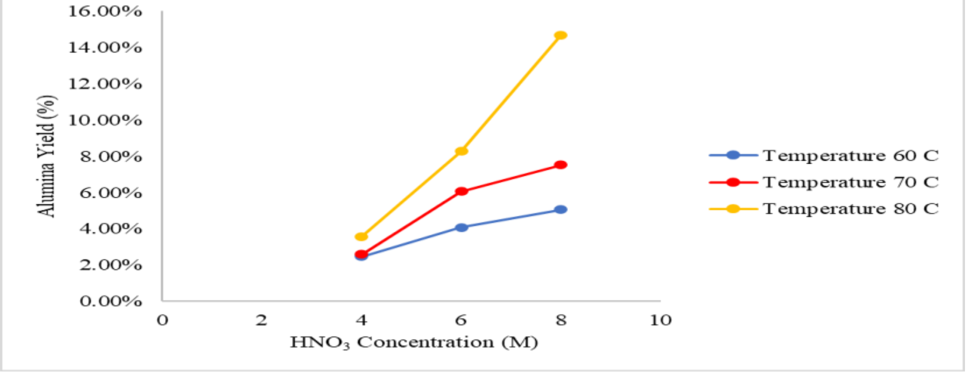

Fig. 5. Effect of HNO_3 concentration on alumina yield

Based on Figure 4 and 5, the result indicates that increasing the acid concentration increases the yield of alumina. In this study, the highest alumina yield was achieved at acid concentration of 8 M, for both HCl and HNO_3,which was 20.06% and 14.69%, respectively.

Based on previous studies, an increase in acid concentration can enhance the yield of alumina. Concentration of H^+ ions affected the solubility of Al atoms. The higher the acid concentration, the higher H^+ ions are contained [10]. It is also assumed that the diffusion rate of Al^{3+} ions from solid to solution increase with an increase in concentration and diffusion of hydronium ions [8]. According to [11], the alumina yield increases because of the acid being predominant at this stage, therefore increasing the conversion of aluminum ions (Al^{3+}) to alumina (Al_2O_3). Based on the level of reactivity to alumina silica, HCl is more reactive than HNO_3. Alumina silica is easily soluble in HCl, both at low concentrations and high concentrations, while alumina can only react with HNO_3 at high concentrations [12].

$$Al_2O_3\ (s) + 6HCl\ (l) \rightarrow 2AlCl_3\ (aq) + 3H_2O\ (l) \quad (1)$$
$$Al_2O_3\ (s) + 6HNO_3\ (l) \rightarrow 2Al(NO_3)_3\ (aq) + 3H_2O\ (l) \quad (2)$$

In this study, the highest alumina yield was achieved at acid concentration of 8 M for both HCl and HNO_3, with respective yields of 20.06% and 14.69%. This indicates that an increase in acid concentration influences the recovery of alumina from Lapindo mud, leading to increased extraction rates and improved process efficiency.

3.3 Effect of Extraction Temperature on Alumina Yield

The extraction process of alumina from Lapindo mud is influenced by temperature. In this study, the extraction process was carried out with two types of acid, which is HCl and HNO_3 at temperatures of 60ºC, 70ºC, and 80ºC. The influence of the extraction temperature on the yield of obtained alumina are shown in Figure 6 and Figure 7.

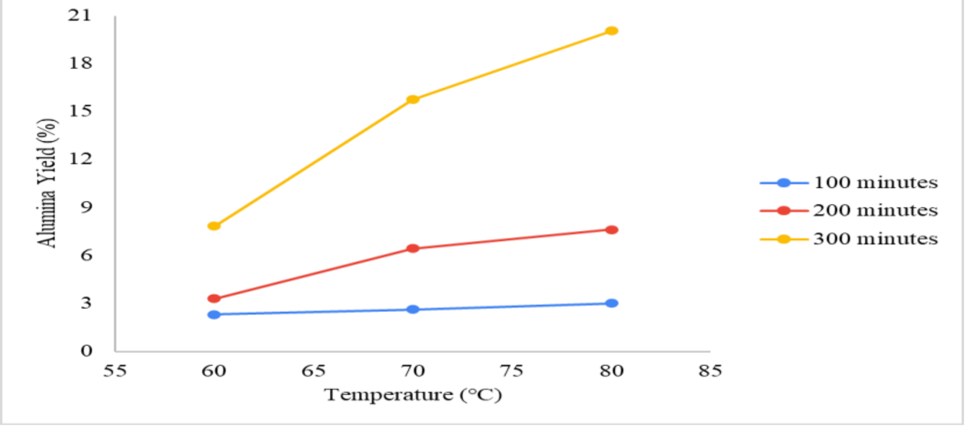

Fig. 6. Effect of extraction temperature on alumina yield for HCl solvent

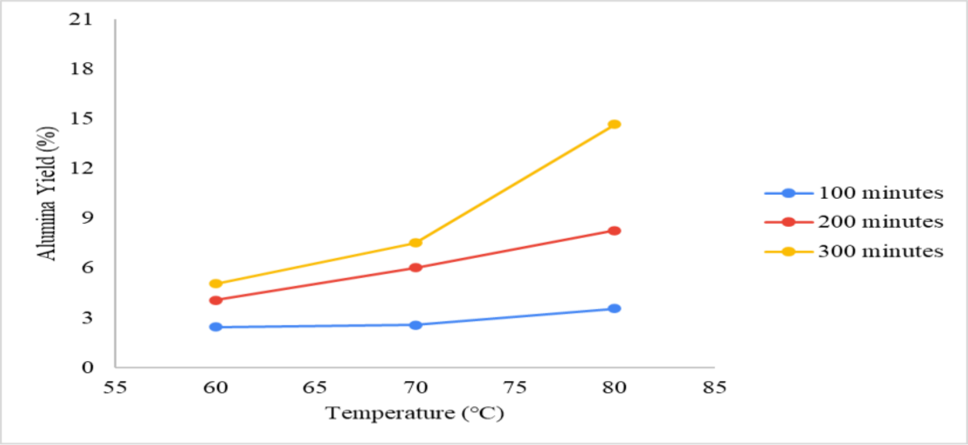

Fig. 7. Effect of temperature on alumina yield for HNO_3 solvent

Based on Figure 6 and 7 above, the result indicates that the highest alumina yield was achieved at extraction temperature of 80ºC, for both HCl and HNO_3, which was 20.06% and 14.69%, respectively.

From the results obtained, it is evident that an increase in extraction temperature leads to a higher yield of alumina. The findings indicate a positive correlation between temperature elevation and the enhanced recovery of alumina from Lapindo mud. As the temperature increases, the extraction rate also rises, indicating a direct influence of temperature on the process efficiency. The significant increase in dissolution rates at higher temperatures is attributed to the exponential relationship between temperature and the constant in the Arrhenius equation, a factor used in calculating the activation energy [13].

Previous studies have shown that elevating the extraction temperature, regardless of the acid used (HCl or HNO_3), can effectively augment the alumina yield. High temperatures boost the kinetic energy of reactant particles, resulting in more energetic and frequent collisions, thereby accelerating the overall reaction rate. Additionally, temperature alterations influence the solubility of specific compounds present in Lapindo mud. Increased temperatures enhance solubility, accelerate the diffusion rate between extraction components, and facilitate particle movement, potentially enhancing the overall extraction yield [14].

In this study, the highest alumina yield was achieved at 80ºC for both HCl and HNO_3, with respective yields of 20.06% and 14.69%. This indicates that an elevation in extraction temperature notably influences the recovery of alumina from Lapindo mud, leading to increased extraction rates and improved process efficiency. Overall, these findings underscore the pivotal role of temperature in enhancing alumina yield and its profound impact on the extraction process from Lapindo mud, as indicated by previous studies.

3.4 XRF Analysis of Alumina and Lapindo Mud

XRF analysis was conducted to identify the major element and minor element from alumina and Lapindo mud. The element from alumina and Lapindo mud was obtained from the collision of atoms on the surface by X-ray. The results of XRF analysis of alumina and Lapindo mud are presented in Table 2 below.

Table 2. XRF analysis results

Element	Lapindo Mud	Alumina with HCl Solvent	Alumina with HNO_3 Solvent
Al_2O_3	16.2%	27.3%	42.8%
SiO_2	36.9%	0.074%	0.273%
Fe_2O_3	7.20%	0.0137%	0.0256%
Na_2O	0.879%	19.0%	1.66%
SO_3	0.931%	0.256%	0.272%
Cl	0.544%	19.3%	0.759%
K_2O	1.47%	0.120%	0.0348%
CaO	2.06%	0.0183%	0.0188%
Zno	0.0124%	0.0216%	0.0157%

Table 2 shows that the XRF analysis results in changes of the relative weight of the elements between Lapindo mud and alumina samples. The Al_2O_3 element contained in Lapindo mud was 16.2%, which is lower than the samples from the alumina extraction. The sample from the alumina extraction with HCl solvent had 27.3% of Al_2O_3 element, while with HNO_3 solvent had 42.8%. Al_2O_3 element has increased due to impurity elements that do not dissolve during the extraction process, so impurity elements are left behind as residue . Apart from that, some elements experienced a significant loss. This can happen because Al_2O_3 can dissolve in acid solvent and other elements can not dissolve in acid solvent [15].

Based on the XRF analysis, it can be seen that the best type of acid solvent between hydrochloric acid (HCl) and nitric acid (HNO_3) that can be used in extracting alumina from Lapindo Mud is HNO_3. Nitric acid solvent has good selectivity. In addition, the regeneration process is very effective, so it can reduce acid usage by up to 90% [16]. Nitric acid reacts with alkalis, basic oxides, and carbonates to form salts. Because it has oxidizing properties, nitric acid does not release its protons in reactions with metals and the resulting salts that are in a higher oxidized state. This causes the extraction results have high alumina element due to the large amount of impurities left in the residue.

3.5 XRD Analysis of Alumina

XRD analysis was conducted to determine the crystallinity of sample from the alumina extraction with HCl and HNO_3 solvent. The crystallinity of alumina was obtained by using crystallinity index. The results of XRD analysis of alumina are presented in Figure 8 below.

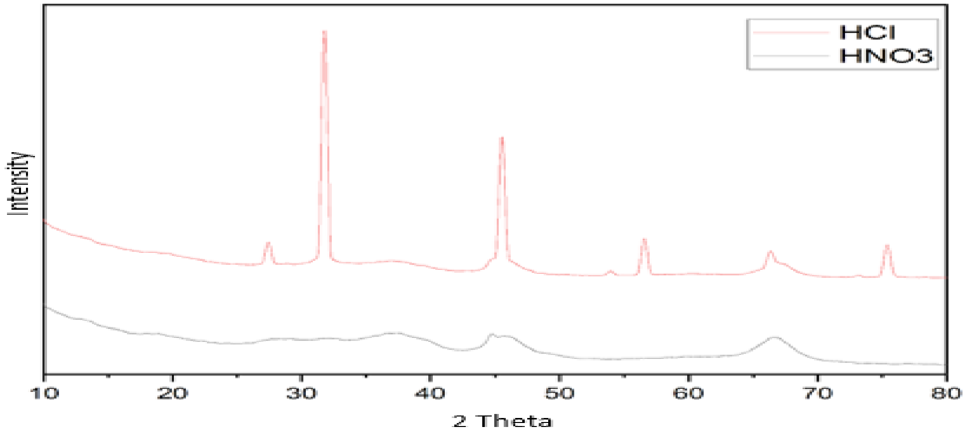

Fig. 8. XRD analysis results

Figure 8 shows that in the XRD analysis result pattern high peaks at 2θ angles for each sample. There are highest peak at 31° for alumina with HCl solvent and at 66° for alumina with HNO_3 solvent. It can be seen that the peaks of alumina with HCl solvent looks sharper and narrower shows that it has high crystallinity. Moreover, the peaks of alumina with HNO_3 solvent looks wider and slopes shows that it amorphous. Alumina with HNO_3 solvent has more reactivity because amorphous has wider surface area and unstable [17].

4 Conclusion

Extraction of alumina from Lapindo mud using acid solvent was successful. Optimum conditions were obtained at acid concentration of 8 M at extraction temperature of 80°C and extraction time for 300 minutes, resulting alumina yield of 20.06% for HCl and 14.69% for HNO_3. Extraction time is one of the factors that will affect the alumina yield obtained because the longer the extraction process, the extraction process will be more perfect. The acid concentration also plays a significant role in extracting alumina from Lapindo mud. The higher acid concentration, resulting in increase of H^+ ions contained and increase of diffusion rate of Al^{3+} ions from solid to solution. The alumina yield also increases because the acid being predominant at this stage. The extraction process of alumina from Lapindo mud also influenced by temperature. Higher temperature resulting in increased solubility, accelerating rate of diffusion between components, and accelerating particle movements. Alumina from extraction using HCl and HNO_3 solvent had a purity of respectively 27.3% and 42.8%. XRD results showed that highest peak for alumina from extraction using HCl and HNO_3 solvent at 31°and 66° respectively.

References

1. Ciptawati, E., Dzikrulloh, M. H. A., Septiani, M. O., Rinata, V., Rokhima, D. A., Azfa F. N., & Sribuana, D. 2022. "Analisis kandungan mineral dari lumpur panas sidoarjo sebagai potensi sumber silika dan arah pemanfaatannya." *Indonesian Journal of Chemical Analysis, 5*(1), 21-23. https://doi.org/10.20885/ijca.vol5.iss1.art3
2. Kusumastuti, H., Trisunaryanti, W., Falah, I. I., & Marsuki, M. F. 2018. "Synthesis of mesoporous silica-alumina from lapindo mud as a support of Ni and Mo metals catalysts for hydrocracking of pyrolyzed α-cellulose." *Rasayan J. Chem, 11*(2), 522-524.
3. Yudhistia, R. A., Triandi, R. T., & Purwonugoho, D. 2018. "Ekstraksi Alumina dalam Lumpur Lapindo menggunakan Pelarut Asam Klorida." Seminar Nasional Inovasi dan Aplikasi Teknologi di Industri, Institut Teknologi Nasional Malang.
4. Maletsky, A. V., Belichko, D. R., Konstantinova, T. E., Volkova, G. K., Doroshkevich, A. S., Lyubchyk, A. I., Burkhovetskiy, V. V., Aleksandrov, V. A., Mardare, D., Mita, C., Chicea, D., Khiemh, L. H. 2021. "Structure formation and properties of corundum ceramics based on metastable aluminium oxide doped with stabilized zirconium dioxide." *Ceramics International, 47*, 19489–19495. https://doi.org/10.1016/j.ceramint.2021.03.286
5. Chua, L. S., Latiff, N. A., Mohamad, M. 2016. "Reflux extraction and cleanup process by column chromatography for high yield of andrographolide enriched extract." *Journal of Applied Research on Medicinal and Aromatic Plants, 3*, 64-70. https://doi.org/10.1016/j.jarmap.2016.01.004

6. Susanty., & Bachmid, F. 2016. "Perbandingan Metode Ekstraksi Maserasi dan Refluks Terhadap Kadar Fenolik dari Ekstrak Tongkol Jagung (Zea mays L.)." *KONVERSI, 5*(2), 87-93. https://doi.org/10.24853/konversi.5.2.87-92
7. Purwonugoho, D., Yudhistia, R. A., & Triandi, R. T. 2018. "Ektraksi alumina dalam lumpur Lapindo menggunakan pelarut asam klorida." *Seminar Nasional Inovasi dan Aplikasi Teknologi di Industri*, 365-369.
8. Sarker. M. S. R., Alam, M. Z., Qadir, M. R., Gafur, M. A., Moniruzzaman, M. 2015. "Extraction and characterization of alumina nanopowders from aluminum dross by acid dissolution process." *International Journal of Minerals, Metallurgy and Materials, 22*(4), 429-436. https://doi.org/10.1007/s12613-015-1090-2
9. Xie, M., Lu, H., Liu, F., & Zhao, H. 2023. "Study on phase transformation and reaction behavior of alumina extraction process by calcification of aluminum dross." *Journal of Material Research and Technology, 25*, 6000-6010. https://doi.org/10.1016/j.jmtr.2023.07.052
10. Ilmi, F. & Mawardi, M. 2023. "Effect of concentration sulfuric acid on alumina extraction from napa soil." *Jurnal Pajar Mipa, 18*(5), 766-770. https://doi.org/10.29303/jpm.v18i5.5546
11. Dadge, K. K. & Onyebuchi, N. C. 2019. "Production of alumina from local clays using nitric acid and acetic acid." *Chemical and Process Engineering Research, 60*, 39-51. https://doi.org/10.7176/CPER
12. Nnanwube, I. A. & Onukwuli, O. D. 2023. "Characterization and kinetics of alumina leaching from calcined Akpugo kaolinite for potential aluminum recovery." *South African Journal of Chemical Engineering, 43*, 24-37. https://doi.org/10.1016/j.sajce.2022.09.014
13. Okwuzu, F. T., Igwegbe, C. A., Okafor, V. N., Ugwu, J. I., & Obi, C. V. 2022. "Kinetics study of alumina leaching from ogbunike clay using hydrochloric acid." *European Journal of Sustainable Development Research, 6*(4), 2542-4742. https://doi.org/10.21601/ejosdr/12395
14. Bariyah, S. & Simatupang, L. 2021. "Activation of Sinabung mount vulcanic ash using various mineral acids." *Indonesian Journal of Chemical Science and Technology, 04*(1), 1-4. https://doi.org/10.24114/ijcst.v4i1.23087
15. Kashcheev, I. D., Zemlyanoi, K. G., & Stepanova, K. O. 2019. "Acidic methods of alumina production (review)." *Refractories and Industrial Ceramics, 60*(3), 237-242. https://doi.org/10.1007/s11148-019-00343-9
16. Yunita, Nurlina, N., & Syahbanu, I. 2020. "Sintesis nanopartikel zink oksida (ZnO) dengan penambahan ekstrak klorofil dari daun suji sebagai sumber capping agent." *POSITRON, 10*(2), 123-130. https://doi.org
17. Putranto, V. H., Kusumastuti, E., & Jumaeri. 2015. "Pemanfaatan zeolit dari abu sekam padi dengan aktivasi asam untuk penurunan kesadahan air." *Jurnal MIPA, 38*(2), 150-159.