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The Influence of Aqua Regia Usage in the Leaching and Extraction Process of Silica from Coal Fly Ash

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ABSTRACT. Waste from coal-burning power stations and other sectors that rely on coal as a source of energy is one of the environmental issues. Fly ash obtained from burning coal causes pollution in the surrounding environment. Subsequently, a great deal of study was conducted on the application of flying ash coal. Among the techniques for making use of the flying ash of coal is the extraction of silica. This study carried out silica leaching using Aqua Regia (a combination of HCl and HNO_3) with various ratios of 1:1, 1:3, and 3:1. The leaching process was carried out at varying temperatures of 30, 45, 60, 75, and 90 °C, with a leaching time of 1 and 2 hours. Precipitates containing silica were analyzed for their levels using XRF. The results of the study show that the ratio HCl:HNO_3 3:1 is able to extract more silica than other solvent ratios.

1. INTRODUCTION

Indonesia is the third-largest coal-producing country in the world after China and India. Total coal production in Indonesia is based on statistical data released by the Geological Agency, Ministry of Energy and Mineral Resources, in 2023, reaching 775 million tons, with 213 million tons for domestic realization (DMO) and 518 million tons for export realization [1]. This causes many power generation industries in Indonesia to use coal as fuel. Steam Power Plant (PLTU) activities use coal as fuel, producing waste in the form of fly ash and bottom ash (FABA) [2]. Coal combustion generates about 80% of fly ash, with bottom ash making up the remaining 20% [3]. The process of burning coal in a PLTU at high temperatures produces fly ash, which is fly ash with a diameter of micrometers [4]. Fly ash is a material produced from the remains of burning coal that is in the form of morphological particles and has pozzolanic properties [5].

In accordance with Government Regulation No. 22 of 2021 Environmental Protection and Management classifies FABA as non-hazardous and toxic waste (non-B3). However, the use of FABA waste in the world is still 25% of the total ash produced, while the remaining 75% is wasted as waste that causes pollution [6,7]. Accumulated waste will cause negative impacts on the environment because it is light and easily carried by the wind into open-air systems, so it can cause environmental pollution.

The Coal Fly Ash typically includes a significant proportion of SiO_2, which may range from 35% to 70% depending on the source of the coal [8]. The extracted silica is promising as an additional photocatalytic in antibacterial applications [9]. Because of that, several researchers have tried to extract silica from various sources with several solvents. Side and Putri compared various acid solvents (HCl, H_2SO_4, and HNO_3) for silica leaching [10]. Salim et al used 0.1 M HCl as a solvent for leaching silica from rice husk and recorded the highest particle purity with 99.99% of SiO_2 content [10]. HCl was also used by Jayanti et al for the extraction of silica from palm oil mill fly ash[11]. In this study, a combination of HCl and HNO_3 was used as a solvent for the leaching process of silica from fly ash.

2. MATERIALS AND METHODS

2.1. Materials and Tools

The materials used in this research were fly ash from the Cirebon Power Plant in West Java, HCl, HNO_3, and KOH. The main equipment used is a Buchner funnel, mesh sieve, pH meter, thermometer, and X-ray fluorescence (XRF) for the analysis of silica components.

2.2. Preparation of Coal Fly Ash Sample

The coal fly ash, which serves as the experimental sample, is initially sieved using sieves with sizes of 100 mesh and 150 mesh. The sieved results are then utilized in the sample preparation process. The sample preparation process involves placing 30 grams of fly ash into a beaker and adding 250 mL of hot distilled water at a temperature of 89°C. The mixture is stirred and left to stand for 2 hours. Subsequently, it is decanted and dried in an oven at 110°C for 33 minutes. After that, the prepared sample is analyzed using XRF analysis.

2.3. Leaching Process of Prepared Sample

The prepared sample, weighing 30 grams, is then added to a container containing 180 mL of distilled water. Subsequently, 1M hydrochloric acid (HCl) and 1M nitric acid (HNO_3) are added until reaching pH 1, with variations in the HCl to HNO_3 ratio of 1:1, 1:3, and 3:1. The solution was then stirred for 1 hour. Afterward, the solution is filtered using a Buchner funnel, and the residue is washed with distilled water to remove any remaining hydrochloric acid or nitric acid until the pH of the filtrate is neutral. The residue is then placed in an oven at 110°C for 33 minutes. Repeating the above experiment with variations in leaching times, namely 1 hour and 2 hours, and variations in leaching temperatures, namely 30ºC, 45ºC, 60ºC, 75ºC, and 90ºC. The several samples obtained from the leaching process are then analyzed using XRF analysis to know the silica percentage in the sample.

2.4. Extraction Process

The extraction process begins by weighing 25 grams of fly ash that has already been leached and soaking it in 150 mL of 3M KOH. It is then heated at 90°C with constant stirring for 3 hours and 30 minutes. The solution is filtered using Whatman No. 42 filter paper and then cooled to room temperature. It is then precipitated by adding HCl solution in a 1:1 ratio with distilled water until a pH of 4 is reached. The solution is filtered again using Whatman No. 42 filter paper and washed with distilled water until a pH of 7 is achieved. Aging is then carried out for 12 hours. After that, the solution is filtered, and the residue is dried in an oven at 110°C for 33 minutes to obtain a white precipitate. The several obtained white precipitate is then analyzed using XRF analysis.

3. RESULTS AND DISCUSSION

In this study, the weight of solids containing silica was obtained from the leaching and extraction process of coal fly ash using variations in leaching time, the ratio of acids forming aqua regia, and leaching temperature. Several samples produced were then analyzed using XRF to determine the silica content and other components.

3.1. The Characteristics of Prepared Sample

Before the leaching process, the fly ash that has undergone initial treatment is analyzed using XRF to determine its component content. The analysis results can be seen in Table 1 and Figure 1 below. Based on the data from Table 1, the highest elemental content found is Calcium (Ca) at 62.060% wt, followed by Sulfur (S) at 36.143% wt. Meanwhile, the Silicon (Si) content is at 0.379% wt. The elemental content in fly ash coal can vary depending on the coal source and composition, the ash formation during the combustion process, and the handling and treatment of fly ash. The primary composition of coal fly ash predominantly consisted of SiO_2 (18–68 wt%), indicating its potential for applications in silica-based porous materials [12].

3.2. Effect of Ratio HCl to HNO_3 in the Leaching Process

Analysis was conducted on the results of the leaching process for variations in the ratio of HCl and HNO_3 mixtures, different leaching temperatures, and leaching times of 1 hour and 2 hours. The obtained precipitate results can be seen in Figure 2.

Table 1. XRF Analysis of Fly Ash Preparation Process

Compound	**Concentration**	**Unit**
Na	0,000	ppm
Mg	0,000	ppm
Al	0,547	% wt
Si	0,379	% wt
P	0,281	% wt
S	36,143	% wt
K	544,300	ppm
Ca	62,060	% wt
Ti	155,600	ppm
Cr	2,200	ppm
Mn	135,200	ppm
Fe	0,317	% wt
Cu	5,400	ppm
Zn	52,200	ppm
Ag	0,150	% wt
Sn	143,300	ppm
Sb	46,500	ppm
Te	130,000	ppm
Pb	13,300	ppm
Total	100,000	% wt

Note: with normalization factor (NF) 1,202

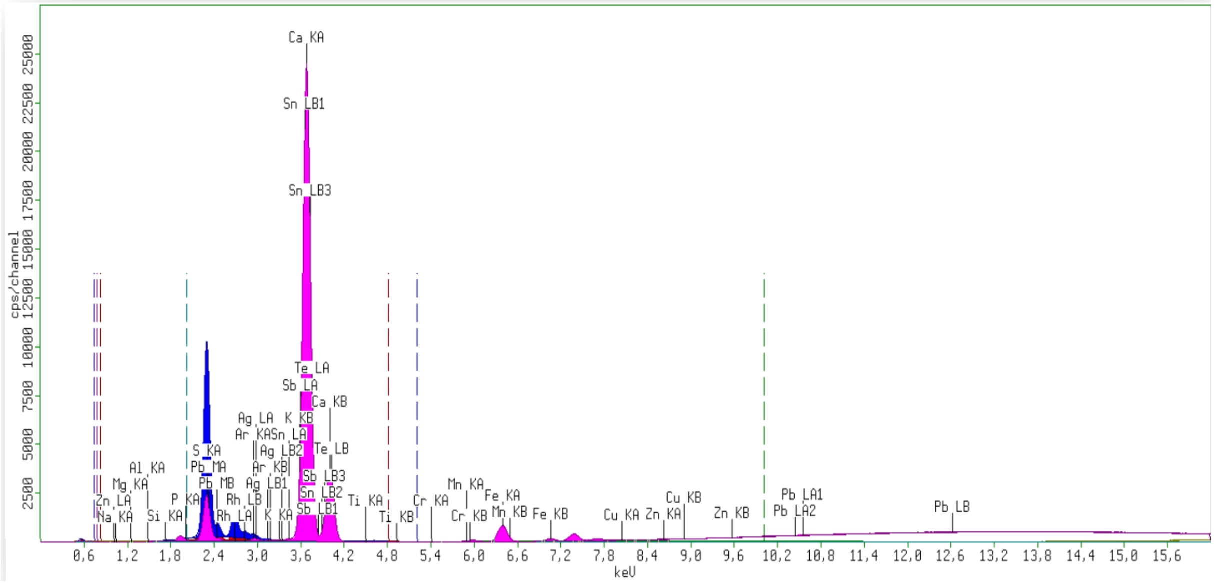
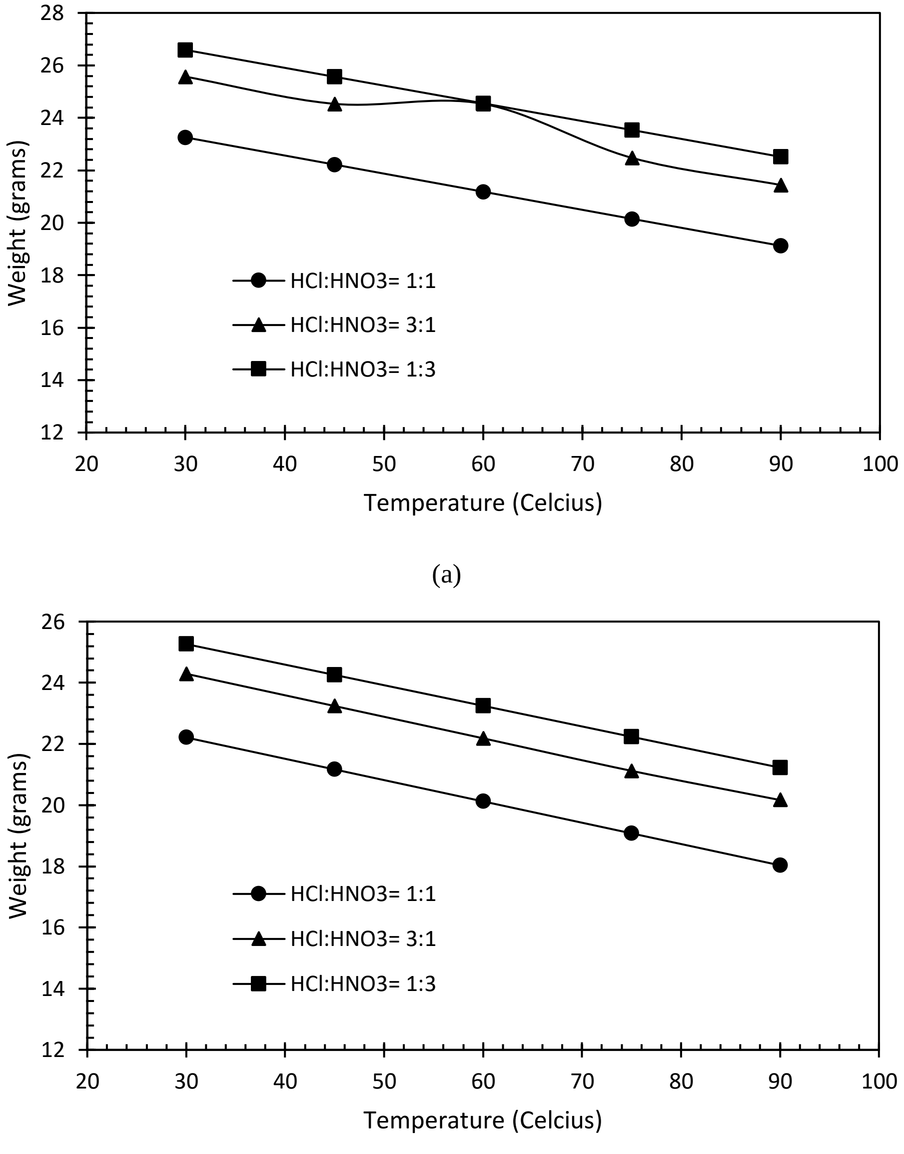


Figure 1. Energy spectrum of the fly ash sample from XRF analysis

The precipitate obtained after 1 hour of leaching had the highest weight of 26.589 grams at a process temperature of 30°C and an HCl to HNO_3 ratio of 1:3. Meanwhile, after 2 hours, the highest precipitate weight obtained was 25.2635 grams at the same temperature of 30°C and the same acid ratio of 1:3. Leaching temperatures higher than 30°C produce less precipitate weight because the main component of the precipitate is Ca so that at higher temperatures it will cause Ca to dissolve in HCl and HNO_3 [13].

XRF analysis was then conducted to determine the content of silica or other metal elements to understand the effect of the HCl and HNO_3 acid mixture on the dissolution of elements. The analysis was performed on four samples at 30°C with leaching times of 1 and 2 hours, and HCl to HNO_3 ratios of 1:3 and 3:1. The contents of silica (Si), aluminum (Al), iron (Fe), phosphorus (P), calcium (Ca), and sulfur (S), which are the major components in fly ash, were examined. A summary of the XRF results can be seen in Table 2.



(a)

(b)

Figure 2. Effect of Ratio HCl to HNO_3 in the Leaching Process at Leaching Time (a) 1 hour, (b) 2 hours

Table 2. The Elemental Composition of Fly Ash Resulting from The Leaching Process

Compound	**Concentration**			
	HCl: HNO_3 (1:3)		**HCl: HNO_3 (3:1)**	
	t= 1 hour	**t= 2 hours**	**t= 1 hour**	**t= 2 hours**
Si	0.282 % wt	0.220 % wt	0.307 % wt	0.305 % wt
Al	0.303 % wt	0.105 % wt	0.378 % wt	0.272 % wt
Fe	0.327 % wt	0.234 % wt	0.270 % wt	0.248 % wt
Ca	64.757 % wt	60.233 % wt	61.732 % wt	60.497 % wt
P	0.383 % wt	0.305 % wt	0.384 % wt	0.304 % wt
S	38.471 % wt	30.695 % wt	38.058 % wt	30.695 % wt

The ratio of HCl to HNO_3 in the aqua regia mixture significantly affects the leaching process of components in coal fly ash. An acid mixture with a higher ratio of HCl dissolves elements with high metallic properties, such as Fe, more effectively. In contrast, weak metals and non-metals like Si, Al, P, Ca, and S dissolve more in mixtures with a higher ratio of HNO_3. This is consistent with previous research, which shows that HCl can dissolve up to 90% of Fe, with higher HCl concentrations resulting in more Fe being dissolved[14]–[16]. Based on Table 2, the high amount of precipitate obtained is due to the significant content of elements that have not yet dissolved during the short leaching time.

3.3. Effect of Ratio HCl to HNO_3 in Leaching to the Extraction Process of Silika

The samples from the leaching process were then extracted using alkali to determine the amount of silica extracted from the fly ash. The results of the silica extraction can be seen in Figure 3.

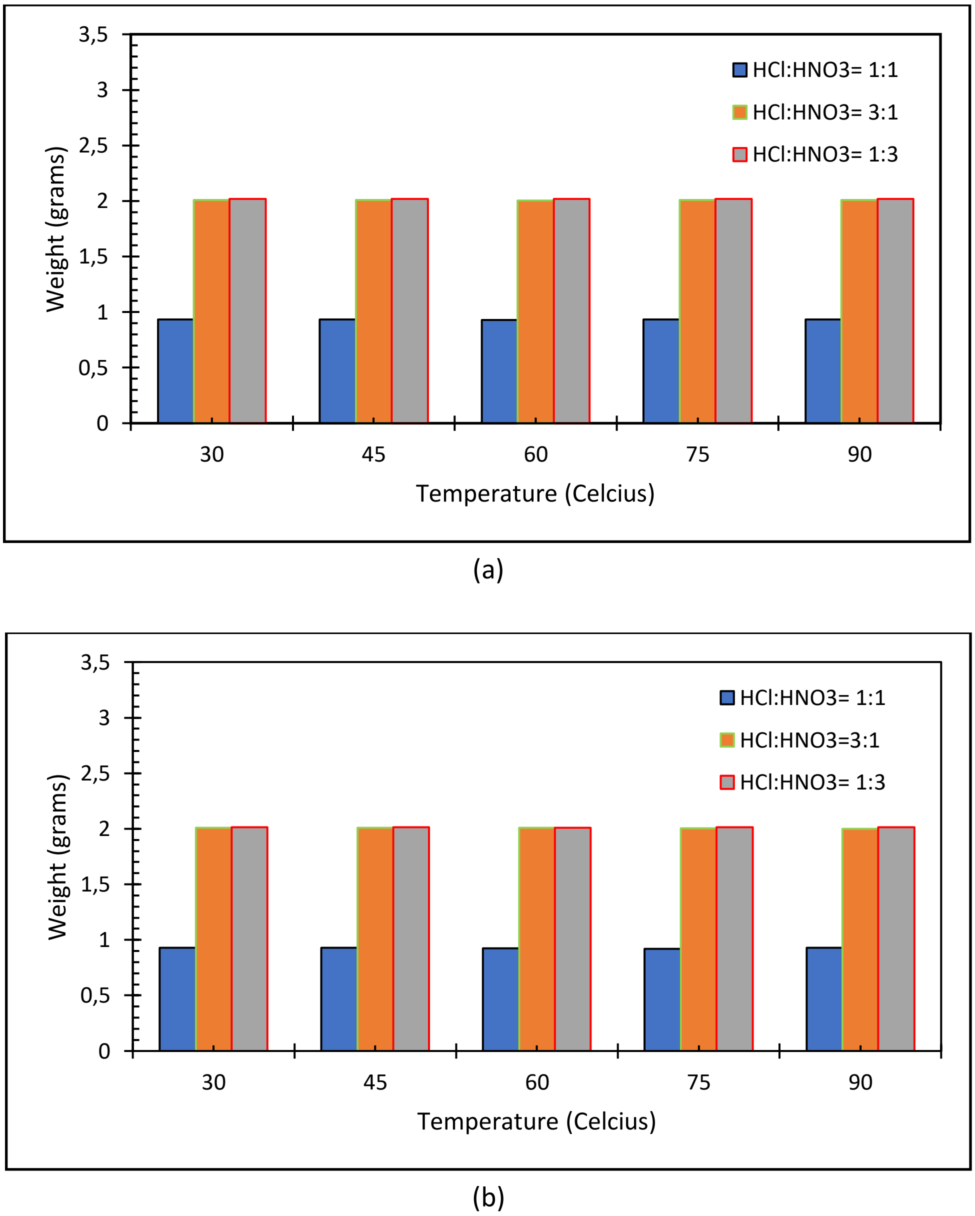


Figure 3. Effect of Ratio HCl to HNO_3 using in Leaching Process to the Extraction Process of Silika, (a) 1 hour of Leaching time, (b) 2 hours of Leaching time

Based on the graph above, the weight of the white silica precipitate is the highest at approximately 2 grams across various leaching temperatures and times. The HCl to HNO_3 acid ratio yields the same weight of white silica precipitate for both the 1:3 and 3:1 ratio. This could be due to silica's chemical stability and its relatively low reactivity compared to other components in the fly ash, which means that both acid mixtures are equally effective in dissolving and precipitating silica. This consistency might also suggest that the fly ash has a fixed amount of extractable silica that reaches saturation quickly under the given conditions, leading to a similar amount of precipitate regardless of minor variations in the leaching process parameters.

XRF analysis was then conducted to determine the content of silica or other metal elements in the extraction result sample. A summary of the XRF results can be seen in Table 3.

Table 3. The Elemental Composition of Fly Ash Resulting from The Extraction Process

Compound	**Concentration**			
	HCl: HNO_3 (1:3)		**HCl: HNO_3 (3:1)**	
	t= 1 hour	**t= 2 hours**	**t= 1 hour**	**t= 2 hours**
Si	0.091% wt	0.420 % wt	0.187 % wt	2.625 % wt
Al	0.000 % wt	0.230 % wt	0.061 % wt	6.337 % wt
Fe	0.049 % wt	0. 328 % wt	0.058 % wt	1.466 % wt
Ca	62.975 % wt	63.181% wt	66.299 % wt	74.639 % wt
P	0.303 % wt	0.224 % wt	0.325 % wt	0.827 % wt
S	34.129 % wt	26.129 % wt	32.090 % wt	13.171 % wt

Based on Table 3, the extract with the highest silica content is obtained under leaching conditions with an HCl to HNO_3 ratio of 3:1, a leaching time of 2 hours, and a leaching temperature of 30°C. In addition to silica, the content of other elements such as Al, Fe, Ca, and P also increased, while the sulfur content decreased. This is likely because a higher ratio of HCl (3:1) creates a more favorable environment for breaking down the fly ash matrix, thus it helps in allowing more silica to dissolve when the extraction process happens. The combination of HCl and HNO_3 can create a strong oxidative and acidic environment, breaking down complex mineral structures and releasing multiple elements into the solution.

4. CONCLUSION

The silica purification process from fly ash is carried out in two stages, namely leaching with aqua regia (HCl:HNO_3) solvent followed by extraction with KOH. The highest silica content was obtained in the leaching process with an aqua regia HCl:HNO_3 ratio of 3:1, which resulted in a white silica precipitate of 24,293 grams with a concentration of silica of 2.625% obtained from XRF analysis.

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