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Potential Application of Microwave-assisted Methods for Metal Extraction from Fly Ash: Review

Tasya Alya Azzahiro^{1,a}, Nita Ayu Setia Ningsi^{1,b}, Susilowati^{1,c}, Renova Panjaitan^{1,d}

¹ Department of Chemical Engineering, Faculty of Technology and Science, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya 60294, East Java, Indonesia

E-mail: ^a22031010016@student.upnjatim.ac.id, ^b22031010023@student.upnjatim.ac.id

*Corresponding author: (renova.p.tk@upnjatim.ac.id) | Phone number: +62

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Abstract

Fly ash is a solid waste product resulting from the combustion of coal or biomass that contains various valuable metals such as Si, Al, Fe, Ca, and Mg. The utilization of fly ash as a source of secondary metals is considered important from both economic and environmental perspectives. Various extraction methods have been applied, including conventional acid leaching, biogenic leaching, alkali leaching, and hydrometallurgy; however, each has limitations regarding efficiency and environmental impact. This study examines the application of a microwave-assisted extraction method that utilizes rapid and uniform heating to enhance the metal dissolution process. Comparative results from various sources indicate that extraction via the microwave method yields higher metal recovery than other methods, such as conventional hydrometallurgical, biogenic, and pyrometallurgical approaches, particularly for aluminium compounds, with recoveries of around 95-96%. The advantages of this method are associated with lower solvent consumption, shorter processing times, higher energy efficiency, and greater environmental friendliness. Thus, the microwave-assisted method is the most effective and efficient technique for metal extraction from fly ash, regardless of the need for further research on industrial-scale applications.

Keywords: Fly ash, hydrometallurgical, metal extraction, microwave-assisted, pyrometallurgical

1. Introduction

Fly ash is a fine-particle solid waste produced in large quantities by the combustion of coal and biomass. This waste consists of inorganic mineral residues that have not been completely burned. Fly ash is produced in large quantities by coal combustion, municipal waste incinerators, and the combustion of biomass such as rice husks and sugarcane bagasse [1]. The main chemical components of fly ash include Si, Al, Fe, Ca, and Mg, with Si and Al being the dominant elements in its composition [2][3][4]. Fly ash also contains heavy metals such as arsenic (As), lead (Pb), chromium (Cr), and mercury (Hg), which are toxic and have the potential to contaminate the environment if not managed properly [5].

Methods for extracting metals from solid materials such as fly ash have been carried out in several ways, conventional hydrometallurgical and pyrometallurgical approaches [6]. Hydrometallurgy is the process of extracting metals from solid materials such as ore, tailings, or industrial waste using liquid solvents (typically acidic or basic solutions) through a series of key stages: leaching, separation and purification of metal ions from the solution, and recovery of the pure metal [7]. This process is generally carried out at relatively low pressure and low temperature approximately 200°C [8]. However, hydrometallurgical methods also have several limitations, such as the need for large quantities of chemical reagents and a relatively long leaching

process to achieve high extraction efficiency. In addition, the leaching kinetics in some systems can be controlled by the diffusion of reagents or products within the solid matrix, thereby limiting the rate of metal extraction [9][10]. In hydrometallurgy, impurities are often dissolved along with the target metal, thereby reducing process selectivity and requiring additional separation and purification steps such as solvent extraction, precipitation, or ion exchange. The use of large quantities of chemical solutions, such as acids or bases, can also generate significant amounts of liquid waste, necessitating proper waste treatment to prevent environmental impacts [11]. In contrast, pyrometallurgy is a metal extraction method that uses high temperatures up to 1000 °C to release metals from ash structures, with mechanisms involving structural changes at intermediate temperatures and dominant chemical reactions at high temperatures [12]. This method is widely used in the recycling of lithium-ion batteries (LIBs) because it can process various types of battery components without complex pretreatment [13]. Its advantages include a simple process, ease of scaling for industrial applications, flexibility with various battery chemistries, and the absence of a pretreatment step [14]. However, pyrometallurgy has drawbacks such as high energy consumption, the inability to selectively separate metals (e.g., in the pyrolysis process), the need for expensive equipment, and the potential to produce hazardous and explosive gases that negatively impact the environment if not properly managed [15].

As a solution to the limitations of hydrometallurgical and pyrometallurgical methods using conventional heating, extraction methods utilizing microwave technology have been developed and are increasingly being applied in the extraction of metals from solid materials such as fly ash [16][17][18]. For instance, in a study conducted by Gunes in 2019, the Microwave-Assisted Extraction (MAE) method was applied to extract rare earth elements from coal fly ash, where the use of microwaves was able to improve extraction efficiency and accelerate the process compared to conventional heating methods [19]. Additionally, in a study conducted by Kai in 2020, the MAE method was also applied to the extraction of arsenic and selenium from fly ash; in this process, the MAE method accelerated the release of metals from the solid matrix, thereby shortening extraction time and improving extraction yields [20]. In this process, the

microwave method utilizes wave technology to heat the mixture of solvent and solid rapidly, unlike conventional conduction methods. The advantages of this method include the efficient process compared to other conventional methods, such as faster extraction times, more economical solvent use, and its ability to penetrate into materials, thereby accelerating chemical reactions with lower energy input [21]. In addition, the microwave-assisted method is classified as a green technology because it reduces waste and operates at relatively low temperatures and pressures, making it safe [22]. Several studies have shown that the microwave method can increase the dissolution rate and enhance the extraction yield of metals such as aluminum (Al) and silica (Si) from fly ash [23][24][25][26].

Therefore, this study aims to compare various methods for extracting metals from fly ash as reported in the literature. By examining the results of previous studies, it is hoped that insights can be gained into the application of microwave technology in the extraction of metal compounds, in terms of process efficiency, energy consumption, and environmental impact. This study is also expected to serve as a reference for further research and to support the utilization of fly ash as a more valuable source of metals, particularly through the application of the Microwave-Assisted Extraction (MAE) method.

2. Characteristics of Fly Ash

Fly ash is typically a powdered solid made primarily of unburned carbon, metal oxides, and other inorganic substances [27]. Morphologically, fly ash is dominated by spherical particles with an amorphous (glassy) structure, which form during the combustion process at high temperatures, thereby influencing physical and chemical properties [28]. However, in addition to spherical particles, fly ash also contains a small number of irregularly shaped particles as well as other mineral fragments [29].

In addition, fly ash also exhibits distinctive morphological forms such as cenospheres and plerospheres, which are spherical particles that are hollow or contain other particles within them [30]. Mineralogically, fly ash consists of an amorphous phase in the form of aluminosilicates and a crystalline phase comprising minerals such as quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), and iron oxides like

hematite (Fe_2O_3), which are the primary components resulting from mineral transformation during the coal combustion process [31].

Fly ash can be produced by various types of combustion processes, such as the combustion of coal [32], paper waste [33], biomass [34], municipal solid waste [35], and heavy fuel oil [36]. The composition of fly ash varies depending on the feedstock and the combustion process used. To provide a more detailed overview of the metal content from various sources of fly ash, this information is presented in Table 1.

Table 1 Type of Fly Ash Source and Metal Composition contained.

Metal	Burning Coal [32]	Burning of paper waste [33]	Burning biomass waste [37]	Burning of Manucipal Solid Waste [35]	Burning heavy oil fuel [36]
Al_2O_3	21.34%	2.65%	5.70%	0.568%	5.53%
Fe_2O_3	14.05%	1.78%	3.20%	0.516%	22%
MnO	0.06%	0.01%	0.55%	0.031%	0.19%
SiO_2	-	29.20%	36.30%	1.756%	11.8%
CaO	-	50.88%	16.20%	40.219%	1.66%
MgO	5.18%	0.86%	4.50%	1.040%	0.39%
K_2O	-	0.01%	13.20%	9.089%	1.91%
TiO_2	0.91%	0.01%	0.45%	0.236%	0.2%
ZnO	-	-	-	0.219%	0.14%
BaO	9.52%	-	0.1%	-	0.21%
Na_2O	0.91%	0.30%	1.16%	16.908%	1.91%

Note : The dash (-) signifies unavailable data in the corresponding references

Table 1 illustrates how each type of fuel or waste generates fly ash with distinct components. These distinctions stem from differences in the constituent compounds of each raw material. In coal combustion, the highest components are aluminum oxide (Al_2O_3) at 21.34% and iron oxide (Fe_2O_3) at 14.05%, while in paper waste, the highest components are calcium oxide (CaO) at 50.88% and aluminum oxide (Al_2O_3) at 2.65%; for biomass waste, the highest components are calcium oxide (CaO) at 16.20% and potassium oxide (K_2O) at 13.20%; while in municipal solid waste, the highest components are calcium oxide (CaO) at 40.219% and potassium oxide at 9.089%. In contrast, the combustion of heavy oil produces the highest components, namely iron oxide at 22% and aluminum oxide at 5.53%. Based on the data from these sources, it can be determined that the highest aluminum oxide content is obtained from coal

combustion at 21.34%, while the highest iron content is obtained from heavy oil combustion at 22%. Thus, based on this explanation, it can be concluded that each combustion process using different feedstocks will yield the highest component content of varying types. Coal combustion produces the highest concentration of aluminum oxide; this is because coal naturally contains aluminosilicate minerals [38]. During the combustion process, these minerals decompose and react to form new phases such as mullite and an amorphous glass phase rich in aluminum oxide; consequently, this process makes aluminum one of the dominant components in coal fly ash [39]. In contrast, the combustion of paper waste yields fly ash with the highest calcium oxide content, as this stems from the paper raw material itself. In paper production, calcium carbonate (CaCO_3) is used as the primary filler to improve paper quality; consequently, the combustion of paper waste yields fly ash with the highest calcium oxide content [40]. Meanwhile, biomass combustion also produces fly ash with the highest calcium oxide content. The high calcium oxide content in fly ash from biomass is due to the ability of plants to absorb and store calcium in the form of compounds such as calcium carbonate and calcium oxalate. When biomass is burned, organic compounds decompose, while calcium remains and accumulates in the fly ash as CaO, making calcium the dominant element in biomass fly ash [34]. Similar to the combustion of paper and biomass, the combustion of municipal solid waste also has the highest calcium oxide content, this is because the waste being burned contains many materials with high calcium oxide content, such as concrete, ceramics, and food scraps [41]. Additionally, the addition of lime in flue gas treatment systems also contributes to calcium accumulation in fly ash, making calcium oxide the dominant component in municipal solid waste fly ash [42], whereas fly ash from heavy oil combustion contains high levels of iron oxide because this fuel originates from the residual fraction of petroleum processing, which has a high iron content [43]. During the combustion process, the organic components in the oil are completely burned, while metal compounds accumulate in the fly ash; iron (Fe) is then converted into oxides such as Fe_2O_3 , making its content dominant in fly ash from heavy oil combustion [36]. Based on the composition of these various combustion sources, the average components found in all combustion processes

include aluminum oxide, iron oxide, manganese oxide, magnesium oxide, potassium oxide, calcium oxide, and titanium oxide. This variation indicates that the type of fuel or waste being burned significantly influences the composition of the resulting fly ash.

By understanding its constituent components, fly ash can be utilized more effectively according to its characteristics [44]. As shown in Figure 1, fly ash with high aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) content has the potential to be used as a coagulant or adsorbent because these oxides

performance of construction materials [46]. Fly ash can also be utilized based on its other physical and chemical properties; for example, fly ash with high pozzolanic properties can be used as a partial cement substitute in concrete because it reacts with calcium hydroxide to form binding compounds that enhance the strength and durability of construction materials, while simultaneously reducing carbon emissions from cement production [47]. On the other hand, fly ash with specific chemical characteristics, such as alkali mineral content, can also be utilized in agriculture to improve soil



Fig. 1. Fly ash utilization based on its characteristics

provide active sites for the binding of metal ions in wastewater treatment [27]. Additionally, fly ash rich in silica (SiO_2) and alumina (Al_2O_3) can be utilized for the synthesis of porous materials such as geopolymers, as its aluminosilicate structure supports the formation of a pore network and high adsorption capacity [45]. On the other hand, fly ash can also be applied as a construction material, such as in concrete or mortar, because its fine spherical particles and chemical composition affect fluidity, reduce water demand, and increase long-term compressive strength, thereby improving the

properties, such as increasing soil pH and nutrient availability, thereby potentially enhancing plant growth when applied appropriately [48].

3. Metal Extraction from Fly Ash

Fly ash contains a variety of elements, including heavy metals and hazardous compounds, which have the potential to contaminate soil, water, and air if not properly managed [49]. Although the presence of fly ash often causes environmental problems, it can actually be utilized for high-value applications. Its relatively high metal content makes

fly ash a potential source of aluminum and other strategic metals [50]. Various extraction methods have been developed to recover valuable metals from fly ash [51]. Table 2 presents several extraction methods that can be used to separate metals from fly ash.

Table 2. Methods for extracting metals from fly ash

Method	Metal	Operating conditions	Results	Reference
Conventional method using HCl as a solvent	Al and Fe	a.T (temperature) = 100 ° C b. Kection of stirring = 300 rpm c.Concentration HCl = 220 g/L (20-22%) d. Liquid solid ratio (S: L) = 1: 10	Fe: 52% Al: 3,7%	[52]
Biogenic Fe(3+) and H ₂ SO ₄ method	Al and Ce	a.T (temperature) = 30 ° C b. Rasio Mass: Pyrite/A-CFA = 1.5: 1 pulp density = 20 g/initial lph bioleaching = 1.75	Al: 91.2% Ce: 63.4%	[53]
Extraction with the alkali method	Al	a.HCl concentration = 1.5 mol/L b. Temperature extraction = 85 ° C c.Extraction time = 120 minutes of liquid-solid = 20: 1	Al: 90%	[54]
Hydrometallurgi method	Al and Fe	a.Concentration H ₂ SO ₄ = 2 m b. Temperature extraction = 100 ° C c.Time = 120 MIND d. Irrasio Solid-water = 1:10	Al: 88,8% Fe: 88,5%	[55]
Extraction method with solvent H ₂ SO ₄	Al and Fe	a.Extraction time = 180 minutes b. Temperatur = 220 ° c.Concentration of sulfuric acid = 3 mole/L	Al: 82,51%	[56]
Microwave method	Al	a.High-alumina fly ash (hafa) /nc mass ratio = 1: 1 b. Temperature (T) = 700 ° C c.Extraction Time = 20 minutes	Al: 96%	[57]
	Al,Ti, Fe	a. Temperature: 280 °C b. Time: 60 minutes c. L/S ratio (liquid/solid): 5:1	Al : 95,5% Ti : 55,6% Fe : 5,6%	[58]
	Al	a. Microwave power: 500 W b. Temperature: 800 °C c. Time: 60 seconds d. Ratio: 1:20	Al : 95,5%	[24]
	Al	A. Power: 600 W b. Temperature: 700 °C c. Time: 30 minutes d. Material ratio: 1:1	Al : 95,9%	[59]

The comparison of extraction methods shown in Table 2 reveals differences in terms of process efficiency, energy consumption, and potential environmental impact. In terms of process efficiency, the microwave-assisted extraction (MAE) method generally exhibits higher extraction efficiency and shorter processing times compared to conventional heating methods [60]. This is due to the ability of microwave technology to generate rapid heating within the material matrix, thereby enhancing mass transfer and accelerating the leaching process between the solvent solution and the solid matrix [61]. Research indicated that the MAE method could significantly increase extraction

yield and reduce extraction time compared to conventional methods due to its more efficient volumetric heating mechanism [62][63]. Additionally, the improved extraction efficiency is linked to the microwave's ability to accelerate chemical reactions and enhance the dissolution of metals from mineral matrices or solid waste. In terms of energy consumption, the microwave method is also considered more efficient than conventional heating methods because microwave energy can be directly absorbed by the material, thereby reducing heat loss to the environment. This direct heating mechanism allows the extraction process to reach operating temperatures in a shorter time, thereby reducing the overall energy requirements of the process [63][62]. In addition, shorter processing times and reduced solvent use also contribute to a lower environmental impact of the extraction process. Microwave technology is even reported to be capable of reducing solvent use by 50–80% and lowering process waste compared to conventional extraction methods, making it considered a more environmentally friendly technology and in line with the principles of green chemistry [63]. Therefore, compared to conventional methods, microwave-assisted extraction has greater potential for improving process efficiency while reducing energy consumption and the environmental impact of the extraction process [64].

Furthermore, Table 2 shows that aluminum is the most common compound extracted from fly ash. This suggests that fly ash has emerged as a significant source of aluminum. However, the aluminum recovery rates vary depending on the extraction method used. The highest aluminum recovery was achieved using the microwave method, at 96% [57]. This result aligns with research conducted by Zhang in 2015, which found that the microwave-assisted extraction process on fly ash was capable of releasing up to approximately 95% of the aluminum, demonstrating very high efficiency in the aluminum recovery process. This high recovery rate is attributed to the microwave heating mechanism, which generates volumetric heating, allowing energy to be directly absorbed by the material and accelerating the release of aluminum from the aluminosilicate structure of fly ash [24]. In addition, other studies have shown that the use of microwave heating in the aluminum extraction process from fly ash can achieve an aluminum extraction efficiency of over 90%, as microwaves can accelerate the breakdown of mineral structures and enhance material reactivity during the extraction process [65]. Therefore, the

microwave method shows great potential for achieving high aluminum recovery.

The extraction process using the Microwave-Assisted Extraction (MAE) method can be used to extract metals from fly ash waste originating from various combustion sources, as shown in Table 1. The table shows the initial composition of metal content in the fly ash prior to the extraction process; thus, differences in metal composition among the various combustion sources can influence the resulting extraction efficiency [66]. The MAE method is known to enhance extraction efficiency because microwave heating produces rapid thereby accelerating the release of metals from the fly ash matrix [67]. Although this method can be applied to various types of fly ash, extraction results tend to be more effective for fly ash derived from coal combustion. This is because coal fly ash has relatively higher concentrations of major metals such as aluminum (Al) and iron (Fe) compared to fly ash from other combustion sources [68], as shown in Table 1. These higher metal concentrations result in a greater potential for extractable metals, allowing the MAE extraction process to achieve higher efficiency [69].

4. Benefits and Drawbacks of Microwave Technology for Fly Ash Extraction

Microwave technology is a modern extraction method that utilizes electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz and is widely applied in the extraction of metals from solid materials such as fly ash [70]. This method accelerates the dissolution of metals into solution through volumetric heating, thereby increasing the mass transfer rate [71]. Compared to conventional methods, microwave-assisted extraction (MAE) offers higher extraction rates, shorter processing times, and lower solvent consumption [72]. Additionally, time, energy, and solvent efficiency are key advantages of MAE, as microwave radiation can significantly accelerate the extraction process [73]. Increasing microwave power has also been shown to increase the amount of extracted metal [74]. This method not only improves extraction efficiency and reduces operational costs, but also enhances metal recovery yields, as demonstrated in recent studies on the extraction of coal fly ash with the aid of microwaves, where rapid and uniform heating promotes the breakdown of stable aluminosilicate phases and significantly increases the recovery of aluminum and other valuable metals compared to conventional processes [75], and is more

environmentally friendly due to reduced solvent and energy consumption [76].

Although microwave-assisted extraction (MAE) is effective on a laboratory scale, its application on an industrial scale still faces major challenges in terms of scale-up difficulties, as the distribution of microwaves over large volumes can lead to uneven heating. Besides, complex reactor and magnetron system designs are required to maintain consistent energy transfer [76]. Furthermore, limitations in its applicability to various types of materials, as well as the lack of process standardization on a large scale, also pose barriers to the widespread implementation of MAE in industry, as reported in studies on the challenges of microwave technology in large-scale processes [77].

5. Future Research

Research on the extraction of metals from fly ash using the Microwave-Assisted Extraction (MAE) method is still limited, so there is considerable room for further development. Going forward, research could focus on the effects of microwave power, heating duration, temperature, and acid solution concentration to determine the optimal conditions for releasing metal ions. Based on the limited previous research, it is necessary to conduct a broader variation of power and duration in order to obtain more comprehensive results. Furthermore, future research could also compare the Microwave-Assisted Extraction (MAE) method with conventional methods in pilot and industrial scale to determine the advantages and energy efficiency of the MAE method in extracting metal content from fly ash.

6. Conclusions

This review has represent that fly ash contain various valuable metals, such as Si, Al, Fe, Ca, and Mg, which have significant potential for recovery as a source of secondary metals. A comparison of several methods shows that the efficiency of metal extraction is highly dependent on the technique used. Among the various approaches available, the microwave-assisted extraction method yielded the most optimal results, with aluminum recovery roughly 95-96%, which is higher than conventional method. The advantage of the microwave method lies in its rapid mechanism, which enables it to increase the rate of metal dissolution, reduce the use of solvents, shorten processing time, and be more energy-efficient. However, further research on pilot and industrial-scale applications of metal

extraction using microwave-assisted method is required. Besides, complex reactor and magnetron system designs are required to maintain consistent energy transfer.

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