

STUDY OF THE CHEMICAL COMPOSITION OF FLY ASH: IMPLICATIONS FOR SUSTAINABLE CEMENT PRODUCTION

NGHIÊN CỨU THÀNH PHẦN HÓA HỌC CỦA TRO BAY: Ý NGHĨA VỚI VIỆC SẢN XUẤT XI MĂNG BỀN VỮNG

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ABSTRACT

This paper investigates the potential of fly ash from coal-fired thermal power plants in Vietnam as a sustainable raw material for cement production. X-ray fluorescence (XRF) analysis revealed that the major oxides - SiO₂, Al₂O₃, and Fe₂O₃ - accounted for 76.07 - 82.00 wt% in four out of five samples, meeting the ASTM C618 Class F criteria for pozzolanic activity. Notably, fly ash from Nghi Son (Sample 5) showed the highest combined reactive oxide content (82.00 wt%) with low CaO (1.83 wt%) and moderate LOI (6.90%), making it highly suitable for high-performance blended cement. The findings highlight the potential of fly ash as a supplementary cementitious material, contributing to resource conservation and the development of high-performance construction materials. This study supports the use of fly ash for producing environmentally friendly and sustainable cement products.

Keywords: Fly ash, XRF, coal combustion, cementitious materials, sustainable construction.

TÓM TẮT

Bài báo này nghiên cứu tiềm năng của tro bay từ các nhà máy nhiệt điện than ở Việt Nam như một nguyên liệu bền vững cho việc sản xuất xi măng. Phân tích phổ huỳnh quang tia X (XRF) cho thấy các oxit chính SiO₂, Al₂O₃ và Fe₂O₃ chiếm từ 76,07 đến 82,00% khối lượng trong bốn trên năm mẫu, đáp ứng tiêu chuẩn ASTM C618 loại F về hoạt tính pozzolan. Đáng chú ý, tro bay từ Nhà máy Nghi Sơn (mẫu số 5) có hàm lượng tổng các oxit hoạt tính cao nhất (82,00% khối lượng), hàm lượng CaO thấp (1,83%) và độ hụt khối khi nung (LOI) trung bình (6,90%), làm cho nó đặc biệt phù hợp để sản xuất xi măng phối trộn hiệu suất cao. Các kết quả này làm nổi bật tiềm năng của tro bay như một vật liệu xi măng bổ sung, góp phần bảo tồn tài nguyên và phát triển các vật liệu xây dựng hiệu suất cao. Nghiên cứu này góp phần khẳng định việc sử dụng tro bay để sản xuất các sản phẩm xi măng bền vững và thân thiện với môi trường.

Từ khóa: Tro bay, XRF, đốt than, vật liệu xi măng, xây dựng bền vững.

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1. INTRODUCTION

The increasing reliance on coal-fired power generation has resulted in a substantial accumulation of coal combustion byproducts, particularly fly ash. Fly ash is a fine particulate material captured from flue gases by electrostatic precipitators or other control devices during the combustion of pulverized coal. Although traditionally

treated as industrial waste, fly ash contains high proportions of silica, alumina, and iron oxide, giving it significant pozzolanic properties and potential for reuse in the construction industry, particularly as a supplementary cementitious material (SCM) [1-3].

In Vietnam, coal remains the dominant energy source, accounting for approximately 49% of the country's

electricity generation [4]. According to national statistics, coal consumption by thermal power plants reached nearly 36.7 million tons in 2020, and continues to rise [5]. Given that the combustion of each ton of coal typically produces 0.1 to 0.2 tons of fly ash, Vietnam generates an estimated 3.6 to 7 million tons of fly ash annually [6]. The disposal of this fly ash poses serious environmental challenges, as current practices primarily involve landfilling or storage in ash ponds, which consume large land areas and can lead to air and groundwater pollution.

To address these challenges, researchers worldwide have investigated the potential reuse of fly ash in various construction materials. In the United States, Class F fly ash has been widely used in concrete production, demonstrating improvements in long-term strength, workability, and durability. According to the American Coal Ash Association (ACAA), over 50% of fly ash produced in the U.S. was beneficially used in 2020, mainly in cement and concrete applications [7]. In Europe, similar trends are observed, with Germany and the United Kingdom integrating fly ash into the cement industry under strict regulatory frameworks. Studies from China and India - two of the largest coal consumers globally have also shown that high-volume fly ash concrete can achieve comparable or even superior performance to conventional concrete mixtures when properly processed [8, 9].

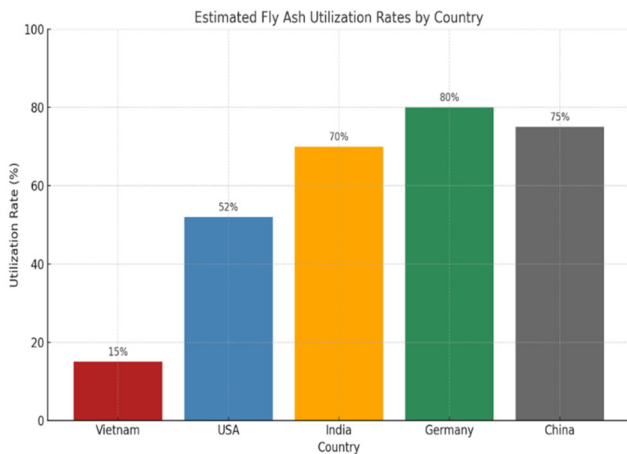


Figure 1. Fly ash reuse rate in some countries [11, 12]

Despite these promising international developments, Vietnam's rate of fly ash utilization remains relatively low. A 2021 report by the Ministry of Construction indicates that only about 15% of fly ash generated in Vietnam is currently being recycled, mostly in cement, unbaked bricks, or road base materials. The rest continues to accumulate, exacerbating environmental and land-use

pressures [10]. Figure 1 shows a clear difference between Vietnam (~15%) and developed countries such as Germany (80%) or China (75%) in fly ash reuse. This highlights the untapped potential in Vietnam.

This study aims to enhance the utilization of fly ash as SCM by providing a detailed chemical characterization of fly ash from a typical coal-fired power plant. X-ray fluorescence (XRF) spectroscopy was used to determine the chemical elemental compositions and evaluate the material's pozzolanic potential. The results of the research provide information on the chemical composition of fly ash and analyze its suitability for cement production. The use of fly ash in SCM will reduce raw material and energy consumption, contributing to CO₂ reduction in production [13]. Using fly ash as an SCM can reduce up to 54% of the CO₂ emissions of concrete production [14]. These researches are completely consistent with the plan to develop clean energy and net-zero emissions in Vietnam.

2. MATERIALS AND METHODS

This study investigates the chemical composition of fly ash samples collected from five different coal-fired thermal power plants across northern and central Vietnam. The objective is to evaluate the pozzolanic potential of fly ash from varied sources, thereby supporting its application as a supplementary cementitious material in the construction industry.

2.1. Sample Collection

Fly ash samples were collected from electrostatic precipitators at five coal-fired thermal power plants operating with different coal sources and combustion technologies. These include:

- **Sample 1:** Na Duong Thermal Power Plant (Lang Son Province)
- **Sample 2:** Son Dong Thermal Power Plant (Bac Giang Province)
- **Sample 3:** Mao Khe Thermal Power Plant (Quang Ninh Province)
- **Sample 4:** Pha Lai 2 Thermal Power Plant (Hai Duong Province)
- **Sample 5:** Nghi Son 1 Thermal Power Plant (Thanh Hoa Province)

Each plant primarily uses bituminous or sub-bituminous coal, sourced from domestic coal mines (e.g., Quang Ninh Basin or Na Duong coalfield). The sampling process was conducted during normal plant operation.

Fly ash samples used for analysis were collected based on the Vietnamese standard TCVN 1693, equivalent to the international standard ISO 13909. Fly ash was collected continuously for 24 hours, once an hour, to obtain a representative composite sample, minimizing short-term variability.

2.2. Sample Preparation

After collection, 5 fly ash samples collected from selected coal-fired thermal power plants were air-dried at room temperature to eliminate residual moisture. The dried samples were homogenized and sieved through a 75 μ m mesh screen to ensure consistency in particle size distribution, as recommended by ASTM C311. Prepared samples were sealed in airtight containers and transported to the laboratory for further analysis.

2.3. Chemical Analysis Using X-Ray Fluorescence (XRF)

The primary method for chemical analysis was X-ray fluorescence (XRF) spectroscopy, selected for its accuracy, reproducibility, and non-destructive nature. The XRF analysis was performed using a PANalytical Axios Max spectrometer, calibrated using certified reference materials to ensure precision. In XRF analysis, the pressed pellet method was used because it is simple, inexpensive, with acceptable accuracy. Each analysis used a sample containing 6g of fly ash and was performed three times with each coal fly ash sample to check the repeatability of the results. To calibrate the XRF analyzer, the SRM2689 standard was used. The error for the main oxides SiO₂, Al₂O₃, Fe₂O₃ is $\pm 1 - 3\%$, alkali oxides Na₂O, K₂O are $\pm 5 - 10\%$, and the number of replicate measurements is three. Due to time and budget limitations, the XRD, SEM, and Blaine analyses have not been performed.

Each sample was analyzed for major and minor oxides, including:

- Silicon dioxide (SiO₂)
- Aluminum oxide (Al₂O₃)
- Iron(III) oxide (Fe₂O₃)
- Calcium oxide (CaO)
- Magnesium oxide (MgO)
- Titanium dioxide (TiO₂)
- Sulfur trioxide (SO₃)
- Potassium oxide (K₂O)
- Sodium oxide (Na₂O)

Additionally, **loss on ignition (LOI)** was determined to assess the amount of unburned carbon and volatile compounds present in each sample, which are relevant

for cement compatibility [15]. The measurement was performed according to ASTM standards; the coal fly ash sample was fired at $950 \pm 25^\circ\text{C}$ for 2 hours. The mass of the samples before and after firing was measured by a balance with an accuracy of 0.00001g.

2.4. Evaluation Criteria

The total content of SiO₂ + Al₂O₃ + Fe₂O₃ was calculated as a key indicator of pozzolanic activity. According to ASTM C618, a total oxide content above 70% qualifies the material as Class F fly ash, suitable for use as a supplementary cementitious material. The chemical data were further compared with international benchmarks, such as EN 450 and other regional studies, to evaluate the comparative quality and usability of Vietnamese fly ash in blended cement production [16, 17].

3. RESULTS

3.1. Chemical Composition of Fly Ash Samples

The chemical composition of the five fly ash samples obtained from different coal-fired thermal power plants in Vietnam was determined using XRF analysis. The major oxide components - SiO₂, Al₂O₃, and Fe₂O₃ - are of particular interest due to their relevance to pozzolanic activity. Table 1 presents the mass percentages of the main oxides detected in each sample. The chemical composition of the five fly ash samples is presented in Table 1, including standard deviations for three replicate measurements.

Table 1. Major Oxide Composition of Fly Ash Samples (wt.% \pm SD)

Oxide	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
SiO ₂	25.85 \pm	43.34	47.62	48.93	51.12
TiO ₂	0.46	0.79	0.79	1.06	1.15
Al ₂ O ₃	14.58	25.87	26.58	21.78	23.71
Fe ₂ O ₃	8.89	6.86	6.84	7.22	7.17
MnO	0.04	0.05	0.05	0.06	0.06
MgO	2.20	2.07	2.32	1.87	1.98
CaO	27.91	3.27	4.50	2.04	1.83
Na ₂ O	1.85	1.41	1.36	1.17	1.21
K ₂ O	1.63	2.21	3.76	3.01	3.82
P ₂ O ₅	0.58	0.17	0.16	0.25	0.30
SO ₃	8.45	2.13	2.34	1.62	0.74
LOI	7.56	11.83	3.68	10.99	6.90
SiO₂/Al₂O₃ (wt ratio)	1.77	1.68	1.79	2.25	2.16

SiO ₂ / Al ₂ O ₃ (mol/mol)	3.01	2.85	3.05	3.82	3.67
Si/Al (mol/mol)	1.56	1.48	1.58	1.98	1.90
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	49.32	76.07	81.04	77.93	82.00

3.2. Discussion of Pozzolanic Potential

Based on the data provided in Table 1, we can analyze the pozzolanic potential of the fly ash samples by considering the oxides' composition, specifically the SiO₂ (silicon dioxide), Al₂O₃ (aluminum oxide), and Fe₂O₃ (iron oxide) content. These oxides are crucial for the pozzolanic activity of fly ash, as they contribute to its ability to react with lime (CaO) in the presence of water, forming compounds that contribute to the strength of concrete. According to **ASTM C618**, fly ash with a combined content of SiO₂ + Al₂O₃ + Fe₂O₃ of **50% or more** is classified as **Class C**, while fly ash containing **70% or more** is classified as **Class F**.

The total content of **SiO₂ + Al₂O₃ + Fe₂O₃** in the samples ranges from **76.07%** (Sample 2) to **82.0%** (Sample 5), meeting the minimum 70% threshold specified in ASTM C618 for Class F fly ash (shown in Figure 2). This suggests that all samples exhibit good pozzolanic potential, suitable for use as mineral additives in cement and concrete production. While sample 1 is just below the 50% threshold for Class C fly ash, so it could be considered for use in applications where moderate strength is required, but it doesn't meet the minimum for Class C.

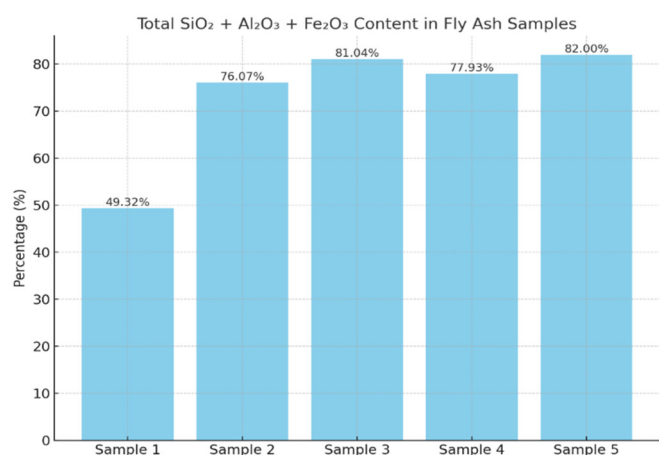


Figure 2. The total content of SiO₂ + Al₂O₃ + Fe₂O₃ oxides in fly ash samples from five thermal power plants

In the cement production process, the chemical composition of materials such as SiO₂ (silicon dioxide),

Al₂O₃ (aluminum oxide), and CaO (calcium oxide) plays an important role in determining the properties of the final product, including strength, workability, and resistance to chemical effects [18, 19]. These oxides directly influence the reaction process in cement production and, in particular, the development of concrete after the cement is mixed with water.

Sample 1 has a relatively high **ratio SiO₂/Al₂O₃** content, but a very high **CaO** content (27.91%). This could lead to the production of cement with high early strength, but may also cause issues with shrinkage and cracking. This sample may be suitable for applications in structures that require high strength in a short period of time. Samples 2 and 3 have relatively high **ratio SiO₂/Al₂O₃** content, which helps improve the pozzolanic potential of the cement, thus producing concrete with high strength and good water resistance. And the low CaO content may reduce the ability to develop early strength, especially in applications that require rapid hardening. Samples 4 and 5, with the highest **ratio SiO₂/Al₂O₃** content, provide strong pozzolanic potential, while their low CaO content helps reduce the risk of shrinkage and heat generation during the early stages of hydration, leading to concrete with long-term durability and good thermal stability. Besides, the Si/Al molar ratio is a critical indicator of the fly ash's potential for geopolymerization. This study, the Si/Al molar ratios of the fly ash samples ranged from 1.48 (Sample 2) to 1.98 (Sample 4). Geopolymers are formed when the aluminosilicate components of fly ash react with alkaline activators to produce a three-dimensional aluminosilicate network. Samples 4 and 5 (Si/Al ≈ 1.9 - 2.0) are expected to produce geopolymers with excellent long-term durability and chemical stability.

The **loss on ignition (LOI)** is an important parameter in evaluating the suitability of fly ash for cement production. The LOI values range from 3.68% to 11.83%. Sample 3 has the lowest LOI (3.68%), suggesting it contains fewer volatile components or unburned carbon. This sample may be better for high-performance concrete applications, as it likely has better pozzolanic properties and lower amounts of impurities. Samples 2 and 4 have relatively high LOI (11.83% and 10.99%), which could indicate a higher amount of unburned carbon or organic material. This may reduce the sample's pozzolanic potential, making it less ideal for high-strength or durable concrete. Samples 1 and 5 have moderate LOI values (7.56% and 6.90%), which suggest

moderate amounts of unburned carbon or organic material. These samples may still be suitable for concrete production, but may need to be monitored for their impact on the concrete's final performance.

Lower LOI values are generally more desirable as they indicate fewer impurities and higher pozzolanic reactivity, while higher LOI values may imply the presence of unburned carbon or organic content, which could reduce the material's effectiveness in cement applications [20, 21]. Although ASTM C618 permits a maximum LOI of 6% for most applications, values slightly exceeding this limit (as seen in Sample 5) may still be acceptable depending on the intended cement formulation and quality control practices.

3.3. Comparison with International Standards

Fly ash from the USA, Europe, and India generally meets the Class F criteria for high-strength applications, while fly ash from China and Brazil also meets the requirements for durable concrete but may have some variations in the rate of early strength development (Table 2).

Table 2. The chemical profiles of fly ash from different countries [16, 17, 21]

Component	Fly Ash from USA (ASTM C618)	Fly Ash from Europe (EN 450)	Fly Ash from India (IS 3812)	Fly Ash from China	Fly Ash from Brazil
SiO ₂	40 - 60%	45 - 60%	50 - 60%	45 - 55%	45 - 55%
Al ₂ O ₃	20 - 30%	20 - 30%	20 - 30%	20 - 30%	20 - 30%
Fe ₂ O ₃	5 - 15%	5 - 15%	5 - 15%	5 - 10%	5 - 15%
CaO	2 - 15%	2 - 15%	1 - 15%	3 - 12%	3 - 12%
LOI	< 6% for Class F, < 12% for Class C	< 6% for high-quality ash	< 12%	< 12%	< 12%
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	≥ 70% for Class F	≥ 70% for Class F	≥ 70% for Class F	≥ 70% for Class F	≥ 70% for Class F

When comparing the SiO₂-Al₂O₃-Fe₂O₃ proportions, CaO, and LOI of the fly ash samples to international standards like ASTM C618, EN 450, and IS 3812, it is clear that the samples show varying levels of pozzolanic potential. Samples 2, 3, 4, and 5 meet the criteria for Class F fly ash, with high SiO₂-Al₂O₃-Fe₂O₃ content (≥ 70%), low CaO, and acceptable LOI values, making them suitable for high-performance concrete applications. Sample 1, with lower SiO₂-Al₂O₃-Fe₂O₃ content and higher LOI, is more

suitable for moderate-strength concrete applications. International Class F fly ash typically contains < 15% CaO. Sample 1 exceeds this limit with 27.91% (+12.91%), while the other samples are well below 5%. This indicates Sample 1 is more reactive at early ages but less durable in long-term chemical resistance.

Compared to fly ash used in the United States, China, India, or Europe, the chemical profiles of the Vietnamese samples are generally consistent in terms of SiO₂-Al₂O₃-Fe₂O₃ proportions. However, the higher variability in CaO and LOI indicates that certain samples may require pretreatment (e.g., beneficiation or carbon removal) to meet stricter specifications for high-performance cement applications. Samples 3 and 5 meet international Class F standards and can be applied directly for: High-performance blended cements with 25 - 35% clinker replacement and geopolymer concrete with minimal pretreatment. Samples 2 and 4, despite meeting the reactive oxide requirement, require LOI reduction to improve compatibility in high-strength or durable concretes. After treatment, they can achieve 20 - 25% clinker substitution. Sample 1, due to its high CaO and low total aluminosilicates, is more appropriate for: moderate clinker substitution (15 - 20%) in Portland-blended cement and applications where early strength development is prioritized over long-term durability.

4. LIMITATIONS OF THE STUDY AND RECOMMENDATIONS FOR FURTHER RESEARCH

The present study focused primarily on the chemical composition of fly ash, as determined through X-ray fluorescence (XRF) analysis. However, other important parameters, such as particle size distribution, specific surface area (Blaine fineness), glass content, and mineralogical phases (assessed via X-ray diffraction, XRD), were not considered, despite their significant impact on the pozzolanic reactivity and overall performance of fly ash in cementitious systems. Additionally, the pozzolanic potential inferred from the oxide composition was not validated through tests such as the strength activity index (SAI), setting time measurements, or durability assessments. Further studies are required to increase the applicability.

Based on the analysis results, coal fly ash sample 1 must be analyzed by XRD to determine the mineral phase; samples 2 and 4 must undergo further in-depth analysis to determine the causes of high LOI. In addition, it is necessary to study and propose solutions to handle substandard fly ash.

Future research should expand the analysis to include mineralogical (XRD), morphological (SEM), and physical property investigations to provide a comprehensive understanding of fly ash behavior in cement and concrete matrices. Moreover, experimental validation through mortar or concrete mixes containing varying proportions of fly ash is essential to confirm its effects on strength development, durability, and long-term performance in real-world applications.

5. CONCLUSION

This study provided a comprehensive chemical characterization of fly ash from five coal-fired power plants in Vietnam to evaluate its suitability as a supplementary cementitious material (SCM) and a potential geopolymer precursor. XRF analysis revealed that the combined content of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ranged from 49.32% (Sample 1) to 82.00% (Sample 5), classifying Samples 2-5 as Class F fly ash according to ASTM C618. Sample 1, with 27.91% CaO and lower reactive oxides, aligns more closely with Class C fly ash. LOI values ranged from 3.68% (Sample 3) to 11.83% (Sample 2), with Samples 2 and 4 exceeding international LOI limits, indicating the need for pre-treatment to remove unburned carbon.

The application of the studied fly ash samples can be categorized based on their chemical properties and potential performance in cementitious systems. Samples 3 and 5, with high reactive oxides (81.04 - 82.00%) and low to moderate LOI (3.68 - 6.90%), are prime candidates for high-quality supplementary cementitious materials (SCMs) and geopolymer precursors, allowing 25 - 35% clinker replacement in high-performance blended cements and geopolymer concrete. Samples 2 and 4, although rich in reactive oxides (76.07 - 77.93%), exhibit high LOI values (~11%), necessitating pre-treatment to reduce unburned carbon before use; after treatment, they are suitable for 20 - 25% clinker substitution in durable concrete and moderate-volume geopolymer applications. Sample 1, characterized by high CaO (27.91%) and low total aluminosilicates (49.32%), is best applied in Portland-blended cements for early-strength development with 15 - 20% clinker replacement, though it is less favorable for long-term durability or geopolymer synthesis.

Overall, 80% of the samples meet or can meet international Class F criteria with minor processing, enabling clinker substitution up to 35% and supporting CO₂ emission reduction in cement production. These

findings highlight the potential of Vietnamese fly ash for sustainable cement manufacturing, geopolymer development, and effective industrial byproduct utilization.

Future studies should include a broader range of analyses, including the evaluation of fly ash's performance in concrete through experimental tests, to fully assess its long-term viability in the construction industry.

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THÔNG TIN TÁC GIẢ

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