

An investigation into the composition of the mineral phase of fly ash using advanced techniques

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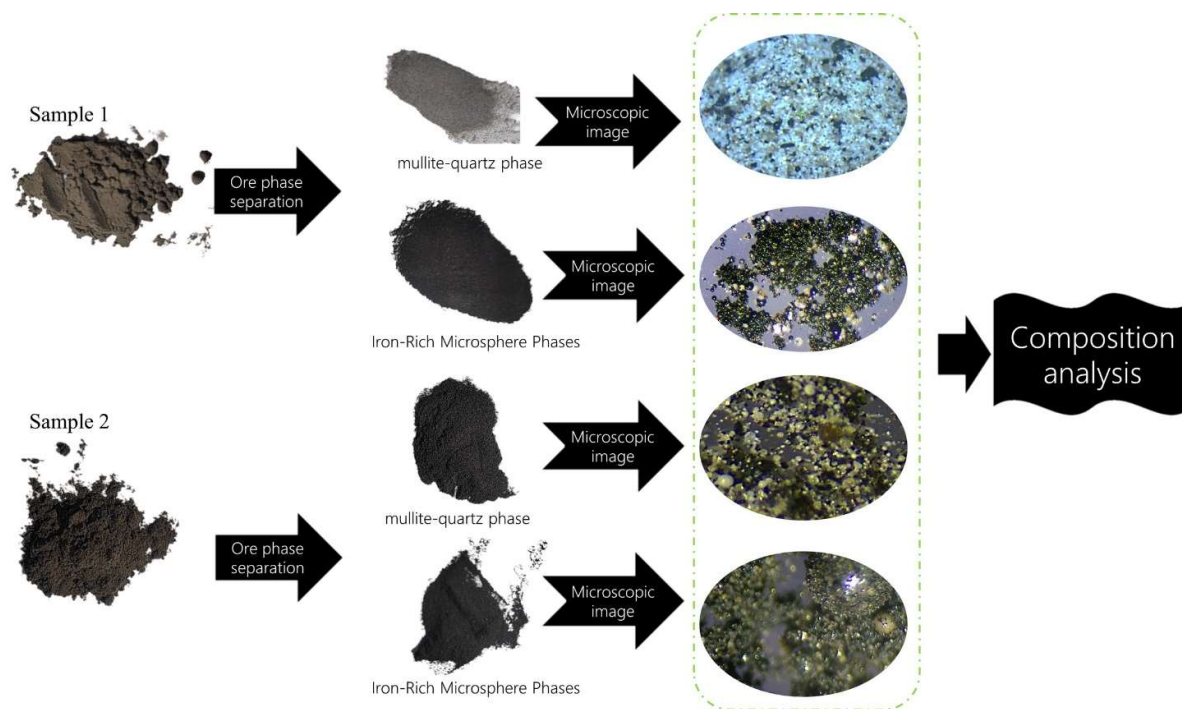
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Graphical Abstract



Abstract

Fly ash, a pivotal byproduct of coal combustion in thermal power plants, has yet to be fully harnessed as an abundant resource for metallic elements resources. A comprehensive understanding of its composition is essential for the exploitation of potentially valuable metals. We research the structural makeup of fly ash utilizing cutting-edge technological approaches, with the aim to provide direction for the development and utilization of its metallic element contents. Micro-Raman spectroscopy, in conjunction with analytical techniques such as X-ray fluorescence spectroscopy, X-ray diffraction, and Fourier-transform infrared spectroscopy, were employed to assess the mineralogical composition of fly ash. The results show that the fly ash analyzed in this study was primarily comprised of mineral phases rich in SiO_2 , Al_2O_3 , and Fe_2O_3 . The primary crystalline phases identified were mullite and quartz. Notably, iron-rich microspheres within the fly ash encompass hematite, magnetite and glassy phases. The mullite-quartz phase also identified the presence of organic carbon. In addition to new knowledge of the mineralogical composition of fly

ash it also demonstrates the potential of micro-Raman spectroscopy in characterization of the mineralogical composition of this material.

Keywords: Fly ash; Mineral phase; Micro-Raman spectroscopy; Thermal power plant

1. Introduction

With the escalating global energy demand, coal remains a pivotal fossil fuel, underpinning power generation and industrial processes. The byproduct of coal combustion, fly ash, is a potential environmental pollution hazard and the potential as a primary resource is ignored (Kumble et al. 2024) . Fly ash is primarily composed of elements like silicon, aluminum, iron, and calcium, and the morphology and distribution of these elements is critical to exploit any potential as a resource (Abbas et al. 2024, Gadore et al. 2024) . However, fly ash exhibits a diverse chemical composition, a complex mineral assemblage, and significantly varying physical properties (Saha et al. 2025) . In fact, various studies have identified approximately 316 minerals belonging to 188 mineral groups in different fly ash samples (Vassilev et al. 2005) . Consequently, conducting a thorough analysis of its mineralogical composition and exploring avenues for its further utilization is imperative to advance sustainable resource management and environmental conservation.

Currently, a range of analytical methodologies, including X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and associated physical separation and chemical leaching techniques, are employed to assess the structural attributes of fly ash. For instance, Bao(Bao 2023) utilized SEM-EDX and XRD to examine the composition of magnetic beads of varying sizes in fly ash. Andrew et al.(Witte et al. 2024) combined SEM-EDS and Raman spectroscopy to scrutinize particle morphology, crystallinity, and the degree of polymerization of the glass phase in fly ash. Chijioke et al. (Egole et al. 2024) characterized two clay deposits in southeastern Nigeria, blended with feldspar and quartz, through chemical analysis, XRF, powder XRD, SEM, and thermal analysis. Niyogi et al. (Niyogi et al. 2018) analyzed the chemical makeup of silicate glass spheres in fly ash using FT-IR and Raman spectroscopy. Tiwari et al.(Tiwari et al. 2014) investigated the properties of raw coal, fly ash, and bottom ash sourced from multiple power plants in India, leveraging XRF and XRD to assess elemental concentrations and calculate enrichment rates. While these characterization methods can indeed reveal the characteristics of fly ash and its mineral compositions, they are not without limitations(Bandopadhyay 2010) . For example, XRD and XRF struggle to gather localized data or conduct analyses at the single-particle level, and they have difficulties in accurately analyzing amorphous phases(Vassilev et al. 2005) . However, Raman micro-spectroscopy offers a potential solution to these shortcomings. Krishna et al.(Polavaram and Garg 2021) successfully employed Raman spectroscopy to quantitatively identify eight secondary phases in cement clinkers with high confidence, including anhydrite, tanzanite, and potassium sulfate. Similarly, Kirkpatrick et al.(Kirkpatrick et al. 1997) used Raman spectroscopy to perform in-depth analyses of complex mineral compositions, identifying significant Raman spectral signals in the wider ranges of 1080 cm^{-1} , $950\text{-}1010\text{ cm}^{-1}$, and $870\text{-}900\text{ cm}^{-1}$, which are strong indicators of

the presence of symmetric stretching vibrations of Q^3 , Q^2 , and Q^1 silicate tetrahedra, respectively. Currently, there is a paucity of research utilizing micro-Raman spectroscopy to analyze the mineral phase composition of fly ash, highlighting the need for further exploration in this area.

We used micro-Raman spectroscopy, in conjunction with other techniques such as XRF, XRD, and FT-IR, to conduct a comprehensive analysis of the composition and structural characteristics of fly ash. The objective being to reveal its chemical composition and also assess the potential of spectroscopic techniques in elucidating the morphology and mineralogical composition of fly ash. Corresponding mineral phases were isolated through mineral phase separation techniques, and spectroscopic techniques were employed to explore the distinctive features of the composition of these mineral phases.

2. Experimental

2.1 Materials

The main reagents used in this study are hydrochloric acid (of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd.) and sodium hydroxide (also of analytical grade, purchased from Aladdin Biochemical Technology Co., Ltd.). Fly ash samples were collected from two power plants in Guizhou Province, China: the Tangzai Thermal Power Plant (hereinafter referred to as M1) and the Zhijin Thermal Power Plant (denoted as M2). The fly ash was obtained following rigorous pretreatment processes, including efficient dust removal, drying in a vacuum oven at 105 °C for 2 hours, and subsequent processing under vacuum for analysis.

2.2 Mineral Phase Separation

This study employed a wet magnetic separation technique to segregate the raw fly ash into

magnetic (iron-rich microspheres) (Dai et al. 2010, Zhang et al. 2019, Hou et al. 2017) and non-magnetic components. Subsequently, a combined acid-base methodology was utilized for the pre-desilication of the non-magnetic components, aiming to isolate the crystalline phase (mullite-quartz phase) present within them. The combined acid-base experiment involved alternating between three alkali and two acid leaching processes, each with distinct conditions. The initial alkali leaching step was conducted at 95 °C, with a solid-to-liquid ratio of 3 mL/g, using a NaOH concentration of 240 g/L for 60 minutes. The subsequent two alkali leaching processes were performed at 80 °C, with a solid-to-liquid ratio of 5 mL/g and a NaOH concentration of 120 g/L, each lasting 60 minutes. The conditions for acid leaching processes were carried out for 60 minutes at 75 °C with a solid-to-liquid ratio of 4 mL/g and an HCl concentration at 2.73 mol/L.

2.3 Analytical methods

The qualitative and quantitative analysis of the major components in fly ash was conducted using a confocal microscope instrument (Finder 930, Zolix Instruments Co., Ltd., Beijing), X-ray fluorescence spectroscopy (AXIOS, Panalytical, Netherlands). To examine the phase structure of the fly ash, X-ray diffraction (D8 Advance, Bruker Technology Co., Ltd.) and Fourier-transform infrared spectroscopy (ALPHA II, Bruker Technology Co., Ltd.) were employed.

Micro-Raman spectroscopy was utilized to measure the Raman spectra of the fly ash, with an excitation wavelength of 532 nm. The sampling points for sample M1 were designated as 1-i (where $i=1, 2, 3, 4$), while those for sample M2 were labeled 2-j (where $j=1, 2, 3, 4$). After the separation of the mullite-quartz phase (denoted as f1 and f2, respectively) from samples M1 and M2, the corresponding sampling points were assigned as f1-i ($i=1, 2, 3$) and f2-j ($j=1, 2, 3$), respectively.

Similarly, the sampling points for the iron-rich microsphere phase (denoted as g1 and g2, respectively), also isolated from samples M1 and M2, were identified as g1-i (i=1, 2, 3, 4) and g2-j (j=1, 2, 3). A simple flowchart illustrating the analytical process is shown in Figure 1.

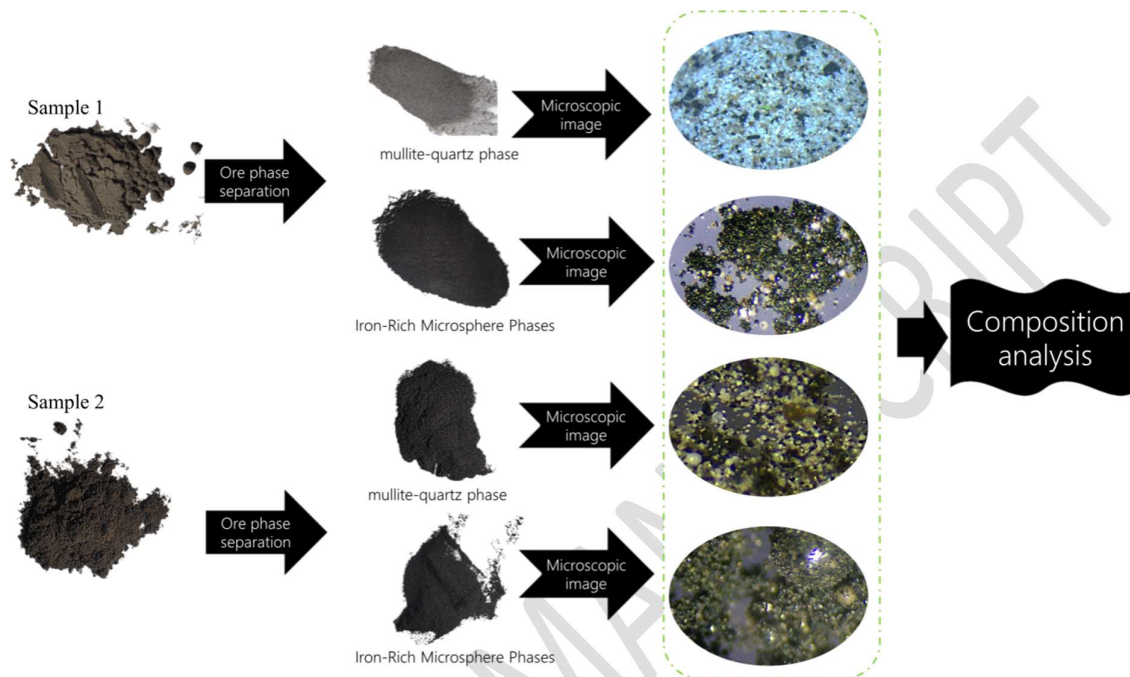


Figure 1. A flowchart showing the application of micro-Raman spectroscopy in the identification of mineral phase composition in fly ash

3. Results and Discussion

3.1. Morphology and Composition Analysis of Fly Ash

In this study, the morphology and elemental composition of fly ash were analyzed by confocal microscopic imaging and SEM-EDS technology, and the elemental and oxide composition of fly ash were further analyzed by XRF. The results are shown in Figure 2 and Table 1.

Figure 2 shows images of two fly ash samples captured at 100x magnification under a confocal microscope (a-b) and SEM-EDS images (c-d). It could be clearly seen from these images that fly

ash was mainly composed of spherical particles. At the same time, due to the differences in coal sources and technological conditions, the element content of fly ash in the two power plants is slightly different. But these spherical particles were rich in oxygen (O), silicon (Si), aluminum (Al), iron (Fe), and carbon (C), along with some small amounts of calcium (Ca) and titanium (Ti). In addition, the particles appear in different colors under light, including translucent tones and some black, gold and deep red particles, indicating the presence of different minerals with different chemical compositions and crystal structures in the fly ash. Upon characterizing the fly ash through XRF analysis, the results were tabulated in Table 1. It was discovered that the fly ash was predominantly composed of SiO_2 , Al_2O_3 , and Fe_2O_3 , which collectively accounted for over 80% of its chemical composition. Specifically, SiO_2 existed in the form of quartz and silicate minerals, Al_2O_3 was commonly found in aluminosilicate minerals, and Fe_2O_3 typically occurred in minerals such as hematite.

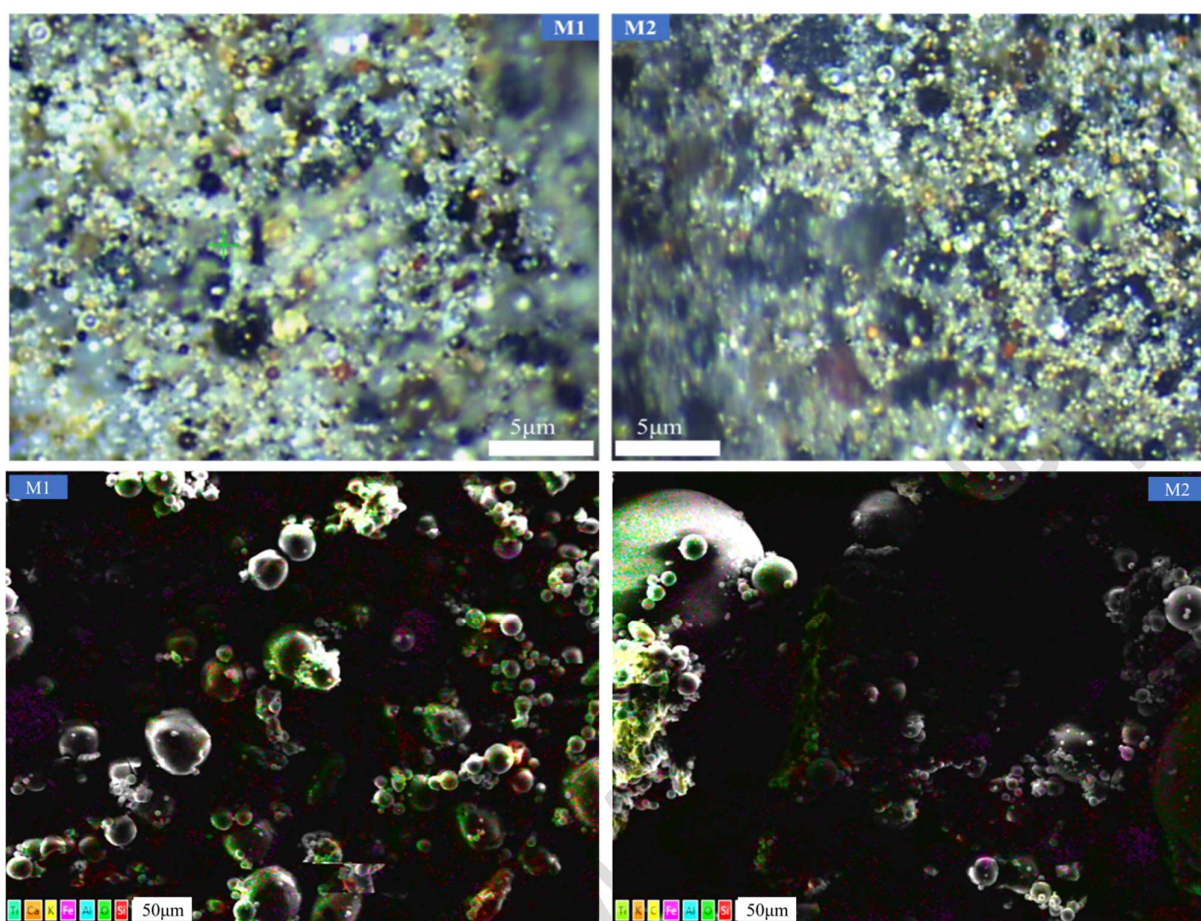


Figure 2. (a)-(b): Microscopic images of fly ash and (c)-(d): SEM-EDS images of fly ash

Table 1. The XRF results of the main chemical ingredients in fly ash

Sample	Ingredients (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	K ₂ O	SO ₃
M1	46.932	29.043	10.71	4.752	2.909	2.558	2.262
M2	48.217	24.312	16.295	2.024	3.961	2.881	1.51

3.2. Basic Structure of Fly Ash

The mineral composition of fly ash is complex, primarily encompassing amorphous phases (chiefly glass phases and residual carbon particles) and crystalline phases (Yan et al. 2018). XRD

analysis provides valuable information on the crystal structure characteristics of various substances. In this study, XRD technology was utilized to examine the crystal structure of two fly ash samples, and the results are shown in Figure 3a.

The primary crystalline phases identified in both fly ash samples were quartz and mullite. Furthermore, a minor quantity of hematite was present in both samples. However, no magnetite peaks were discernible in the spectra, which could potentially be attributed to the low magnetite content in the fly ash thus resulting in a difficulty to test (The content of iron microbeads measured in M1 and M2 fly ash samples were 9.56% and 10.78%, respectively). The study also revealed the presence of a broad peak within the 2θ range of 20° - 30° , accompanied by a high background in the diffraction pattern. This characteristic peak is an indicator showing potential existence of glass bodies, unburned carbon particles, and other uncrystallized oxides within the fly ash (Ward and French 2006, Oiu et al. 2008). Correspondingly, similar broad peaks were observed in the XRD spectra of both fly ash samples in this study.

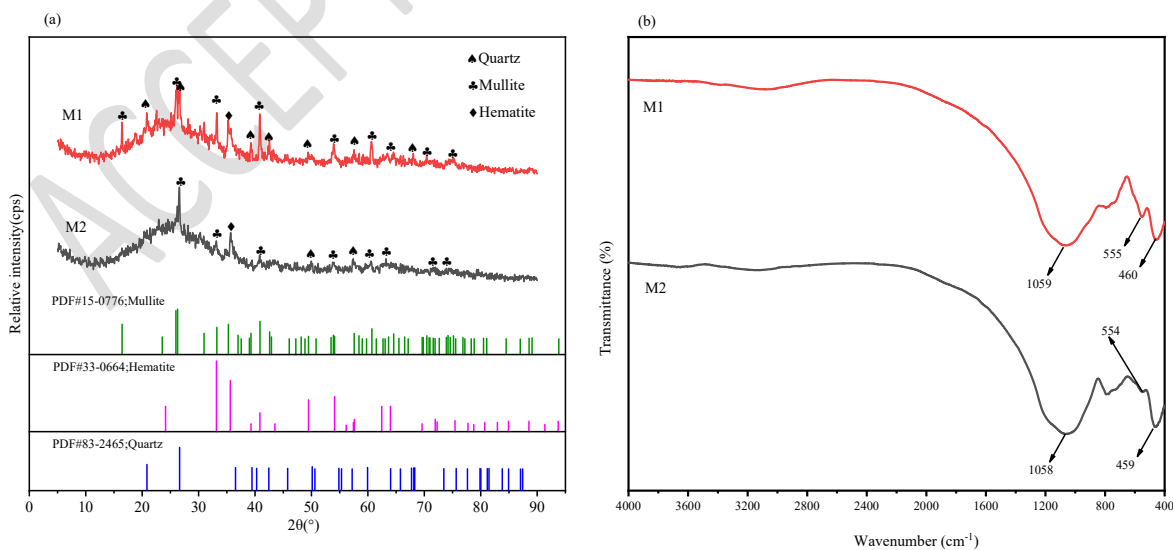


Figure 3. (a) XRD results of fly ash and (b) FT-IR results of fly ash

The XRD analysis conducted above enables the determination of the primary crystalline phase components in fly ash. However, regarding the identification of amorphous states, no definitive pattern for peaks associated with amorphous glass featuring regular atomic arrangements has been established in XRD studies(Kirkpatrick et al. 1997) . Consequently, this study employs FT-IR spectroscopy to more precisely analyze the amorphous phase components present in fly ash. The results are shown in Figure 3b. The FT-IR spectra of the two fly ash samples exhibit considerable similarity, suggesting a comparable composition between them. Each spectrum from each sample shows three distinctive absorption peaks, indicative of internal vibrations within aluminosilicate structures. Specifically, the absorption peaks observed at 460 cm^{-1} for sample M1 and 459 cm^{-1} for sample M2 are attributed to the bending vibrations of Si-O or Al-O bonds(Fernández-Jiménez and Palomo 2005) . The peaks located at 1058 cm^{-1} and 1059 cm^{-1} , respectively, stem from the asymmetric stretching vibrations of Si-O-Si or Si-O-Al linkages(Mozgawa et al. 2014) .Furthermore, the absorption peaks within the $550\text{-}850\text{ cm}^{-1}$ range are influenced by the degree of polymerization of the aluminosilicate structure(Bai et al. 2008) . Notably, the peaks within this region for both fly ash samples in this study are relatively weak, signifying a significant amount and weak polymerization effect of the amorphous phase in fly ash. Therefore, it can be inferred that fly ash contains a substantial quantity of aluminosilicate glass.

3.3. Micro-Raman Spectroscopy Analysis of Fly Ash

3.3.1. Results of Raw Fly Ash

Based on the XRF and XRD analysis data, fly ash is shown to contain a substantial quantity of both crystalline and amorphous aluminosilicates. Figure 4 shows the Raman spectra of two fly ash

samples, with Figures 4(a) and 4(b) displaying the microscopic images of these samples, and Figures 4(c) and 4(d) show the Raman spectra of samples M1 and M2, respectively.

In Figure 4(c), distinct peaks are observed at 468 cm^{-1} , 471 cm^{-1} , 471 cm^{-1} , and 468 cm^{-1} for particles 1-1, 1-2, 1-3, and 1-4 of sample M1. These peaks are likely associated with the vibrational modes of bridging oxygen within the Si-O-Si, Si-O-Al, and Al-O-Al bonds in the tetrahedral structure, as reported in (Xie 2008, Silva et al. 2012). Notably, particle 1-4 exhibits no other prominent peaks besides the one at 468 cm^{-1} , which is attributed to the bending vibration of bridge oxygen in the silicon-oxygen tetrahedron structure commonly found in quartz crystals (Guedes et al. 2008, Pan et al. 2006). Additionally, the Raman spectrum of particle 1-2 displays weak peaks at 781 cm^{-1} and 897 cm^{-1} , with 897 cm^{-1} related to the precise stretching vibration of the Si-O structure. The Raman shift at 781 cm^{-1} may be attributed to the influence of aluminum incorporation into the Si-O structure, causing a shift from the typical $800\text{-}1200\text{ cm}^{-1}$ region to lower frequencies, as discussed in (Pan et al. 2006, McMillan et al. 1982). Furthermore, peaks observed at 333 cm^{-1} and 211 cm^{-1} in particles 1-1, 1-2, and 1-3 are likely due to the bending vibration of the Al-O structure (Xie 2008), indicating that particles 1-1, 1-2, and 1-3 represent distinct aluminosilicate structures.

Figure 4(d) shows the Raman spectra of particles in sample M2, it is noteworthy that based on XRD, XRF, and FT-IR analyses, the compound composition of sample M2 is similar to that of sample M1, comprising a high proportion of amorphous aluminosilicate glasses alongside other crystalline and amorphous components. In particular, the peak at 326 cm^{-1} in particle 2-1 is likely caused by the bending vibration of the Al-O structure. Meanwhile, peaks observed at 467 cm^{-1} , 462

cm^{-1} , and 467 cm^{-1} in particles 2-1, 2-3, and 2-4, respectively, are attributed to the bending vibration of bridging oxygen within the Si-O structure. Peaks at 727 cm^{-1} and 766 cm^{-1} in particles 2-1 and 2-4 are indicative of the symmetric stretching vibration of the Al-O structure (Mysen 1996), while the peak at 909 cm^{-1} in particle 2-3 is possibly caused by the symmetric stretching vibration of the Si-O structure (Xie 2008) [21]. Notably, two distinct broad peaks are also observed at 1344 cm^{-1} and 1582 cm^{-1} in particle 2-2, which have been reported to be associated with unburned amorphous carbon (Guedes et al. 2008).

Overall, the presence of Raman peaks confirms the abundance of aluminosilicate or silicate crystals and amorphous crystals in fly ash, further validating the existence of glass phases and mullite-quartz phases. However, the absence of Raman peaks related to Fe-O structures in these spectra can be attributed to the low content of iron-bearing minerals in fly ash.

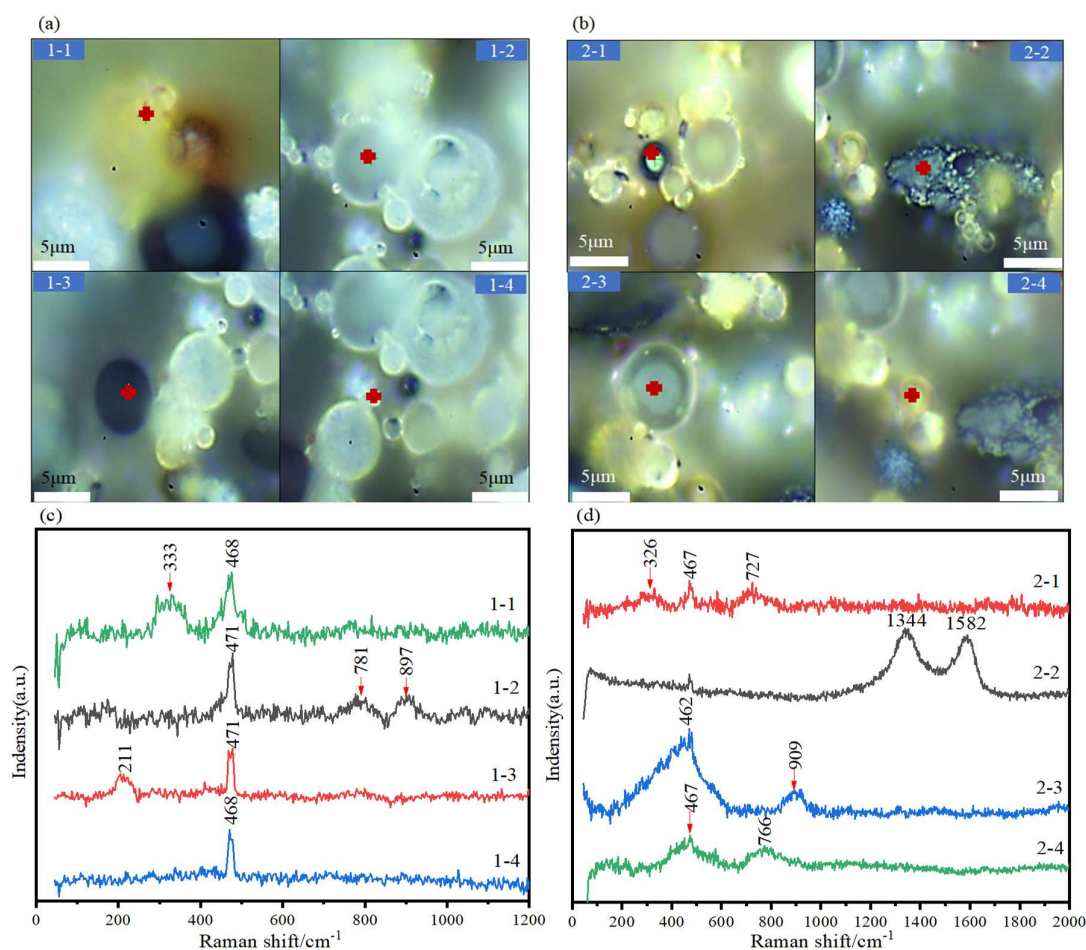


Figure 4. Raman spectra results of fly ash: (a) Tested locations from M1, corresponding to Raman spectra of (c); Tested locations from M2, corresponding to Raman spectra of (d).

3.3.2. Results from the Mullite-Quartz Phase

It has shown that a high proportion of amorphous phases, which can be divided into amorphous aluminosilicate matrix and amorphous silica, along with a small and variable number of crystalline phases (mullite and quartz), constitute the primary components of fly ash (Yan et al. 2018). After the non-magnetic components of M1 and M2 samples in this study were treated with the acid-base pre-treatment method, the amorphous phase was effectively dissolved, and finally crystalline phase substances (mainly mullite and quartz) were obtained. Moreover, the content of crystalline substances accounted for 26.22% and 29.24% respectively, so the content of amorphous

substances was higher.

Figure 5 shows the results of the micro-Raman spectroscopy and XRD spectra of the mullite-quartz phase. Figure 5(a-b) show the locations tested in microscopic images of the mullite-quartz phase (Mf1 and Mf2), corresponding to the Raman spectra shown in Figures 5(c-d). Figure 5(e) shows the XRD spectra of the mullite-quartz phase.

As illustrated in Figure 5(c), the prominent peak observed at 469 cm^{-1} in the Raman spectrum of particle f1-2 from sample M1 is attributed to the bending vibration of bridging oxygen within the silicon-oxygen tetrahedron structure, characteristic of quartz crystals (Silva et al. 2012). In contrast, the Raman spectrum of particle f1-1 exhibits weak peaks at 279 cm^{-1} and 935 cm^{-1} , stemming from the bending vibration and symmetric stretching vibration of the Al-O structure, respectively. Additionally, the peak at 470 cm^{-1} arises from the bending vibration of the Si-O structure. Similarly, in the spectrum of particle f1-3, a sharp peak at 468 cm^{-1} is observed, assigned to the bending vibration of the Si-O structure, while a small sharp peak at 764 cm^{-1} is attributed to the symmetric stretching vibration of the Al-O structure (Pan 2006). The disparities in the Al-O and Si-O structures between particles f1-1 and f1-3 lead to distinct differences in their Raman spectra, suggesting that particles f1-1 and f1-3 are likely mullite crystals with varying crystal structures.

Figure 5(d) shows the Raman spectra of sample M2, a sharp peak at 462 cm^{-1} is evident in the spectrum of particle f2-2. This peak is attributed to the bending vibration of the Si-O structure and corresponds to the characteristic peak of quartz crystals. Furthermore, the Raman spectrum of particle f2-1 exhibits characteristic peaks of amorphous organic carbon at 1344 cm^{-1} and 1590 cm^{-1} ,

along with a peak at 474 cm^{-1} resulting from the bending vibration of the Si-O structure, indicating that this particle is a mixture of silicates and amorphous carbon (Guedes et al. 2008, Moseenkov et al. 2023). Finally, in the spectrum of particle f2-3, a small sharp peak at 477 cm^{-1} signifies the presence of Si-O structures, while weak broad peaks at 336 cm^{-1} and 742 cm^{-1} are indicative of Al-O structures (Xie 2008, Pan 2006), confirming that this particle is a mullite crystal.

Figure 5(e) shows the XRD spectra of mullite-quartz phase of fly ash of two samples. Compared with the XRD pattern of fly ash in Figure 3(a), the characteristic diffraction peak of mullite-quartz phase at $20\text{-}30^\circ$ is significantly weakened, indicating that the glass phase and other amorphous substances in the raw ash are effectively removed after the combined acid-base leaching method. The results show that the main crystal substances in the treated mullite quartz phase are mullite and quartz, which correspond to the results of Raman spectrum analysis above. XRD cannot effectively detect the small impurities in the substance, and for the mineral mixture of fly ash, the composition is more complex, its detection is not effective at this time, but the microscopic imaging in the micro-Raman technology can easily identify the small impurities and trace minerals and generate the corresponding Raman signal. For example, in the Raman spectroscopy, the presence of amorphous carbon was identified, while in the XRD analysis, due to the small content of carbon particles in the fly ash and its high amorphous components it cannot be effectively detected. At the same time, Raman spectroscopy can also provide information about the morphology of elements and symmetry of structures of mullite with different structures. Overall, the micro-Raman spectroscopy analysis of the mullite-quartz phase in two fly ash samples reveals that, upon the removal of the glass phase from the non-magnetic component, the primary crystalline components of fly ash show different structures for mullite and quartz, along with the presence of unburned

amorphous carbon.

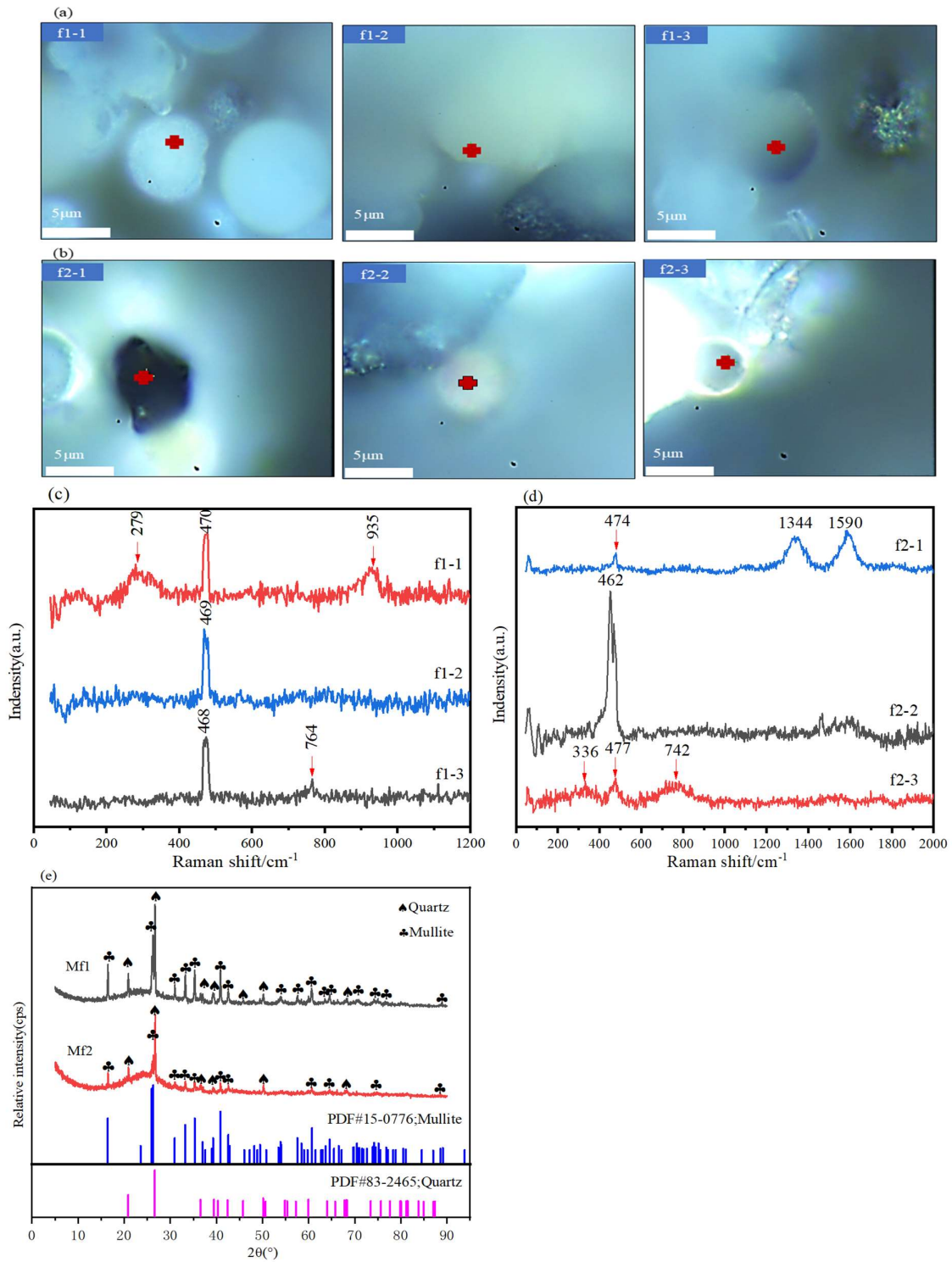


Figure 5. Raman spectra results of fly ash: (a) Tested locations from Mf1, corresponding to Raman spectra of (c); Tested locations from Mf2, corresponding to Raman spectra of (d); (e) XRD results

of mullite-quartz phase in Mf1 and Mf2.

3.3.3. Results of Iron-Rich Microsphere Phase

Research has shown that the magnetic components primarily consist of iron oxides and amorphous silicates (Kutchko and Kim 2006). Figure 6 shows the Raman spectra and XRD spectra of the iron-rich microsphere phase from two samples, where Figures 6(a) and 6(b) show the tested locations in microscopic images of Mg1 and Mg2. Figures 6(c) and 6(d) show the Raman spectra corresponding to above locations in the two samples. The XRD spectra are shown in Figure 6(e).

In Figure 6(c), the Raman spectrum of the iron-rich microsphere phase of sample M1 indicates Raman shifts at 225 cm^{-1} and 286 cm^{-1} in particle g1-1, signifying the bending vibration of the Fe-O structure, which aligns with the characteristic peaks of hematite (Legodi and de Waal 2007, Das and Hendry 2011). Additionally, a sharp peak is observed at 468 cm^{-1} , which is not attributed to hematite's spectrum, possibly indicating the presence of amorphous impurities. It is therefore speculated that this peak arises from Si-O structures. The peak at 473 cm^{-1} in particle g1-2 is attributed to the symmetrical bending vibration of the Si-O structure. The two peaks at approximately 206 cm^{-1} and 264 cm^{-1} are associated with the bending vibration of the Al-O structure, suggesting that these particles may be some form of aluminosilicate crystal or amorphous material (Pan 2006). Particle g1-3 exhibits a broad peak at 665 cm^{-1} , which coincides with the characteristic Raman spectrum of magnetite. However, in natural magnetite, two weak band peaks are typically present at 295 cm^{-1} and 521 cm^{-1} , which are absent in this particle, possibly due to interference from other minerals (Das and Hendry 2011). In particle g1-4, a prominent sharp peak at 470 cm^{-1} is evident, resembling the characteristic peak of quartz associated with the bending

vibration of bridge oxygen. However, the peak frequency here is notably higher than that of quartz, potentially influenced by other mineral components affecting the Si-O bridge oxygen vibration. Overall, the iron microsphere phase comprises a silicate crystal or an amorphous structure.

Figure 6(d) shows the Raman spectrum of sample M2. The Raman spectrum of particle g2-1 in sample M2 reveals several distinct sharp peaks within the 200-1200 cm^{-1} range. Meanwhile, through microscopic Raman images of this particle, we could find that the particles showed a spherical shape, the formation of this type of particle is related to the combustion conditions of coal, coal, and power plant combustion technology. However, the specific composition of this particle could not be determined. The Raman spectrum of particle g2-2 displays distinct peaks at 468 cm^{-1} and 910 cm^{-1} , which correspond to the symmetric bending vibration and non-bridging oxygen symmetric stretching vibration of the Si-O structure, respectively, indicating that this particle may be a silicate glass. For particle g2-3, a sharp peak at 473 cm^{-1} is observed in the Raman spectrum, akin to the spectrum of g1-4 from sample M1, suggesting that this particle may also belong to a certain type of silicate crystal or amorphous material.

Figure 6(e) shows the XRD spectra of iron microbeads of two fly ash samples. It was found that the main crystal structure of the iron microbead phase was magnetite and hematite, and a relatively obvious hump was still found at 20-25°, indicating the existence of glass in the iron microbead phase (Hu et al. 2018), which was consistent with the results of the microscopic Raman analysis. Overall, the analysis of Raman spectra shows that the iron microsphere phase is mainly composed of a composite structure of silicate, aluminosilicate glass, magnetite and hematite.

Table 2 lists the Raman shifts and corresponding structures of each particle in this study. Due

to the complexity of the composition of fly ash, it was impossible to determine the composition ratio of Al, Si and O in aluminosilicate amorphous glass and aluminosilicate crystal. Although the position of Raman peaks of aluminosilicate crystals and amorphous crystals is similar to some extent, the Raman peaks of aluminosilicate crystals (especially mullite and quartz) can be obtained more accurately after the aluminosilicate glass is effectively removed by acid-base combination method. In addition, we observe that the characteristic Raman peak of quartz crystal appears to be around 464cm^{-1} , and no other significant spectral peak is found in this region. As for the identification of iron oxides and unburned amorphous carbon particles, combined with the detailed observation of particle morphology and XRD characterization results provides a more accurate assessment.

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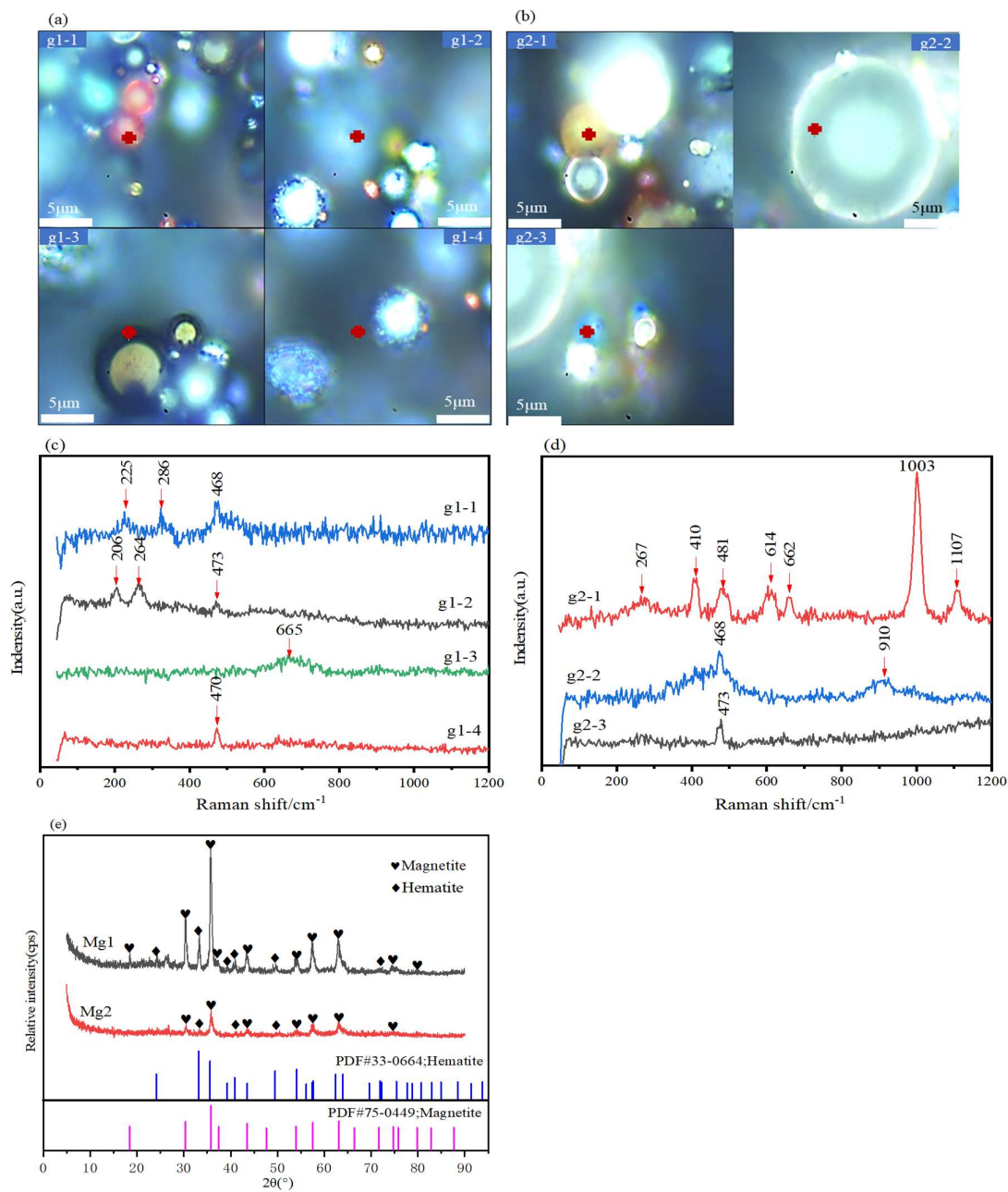


Figure 6. Raman spectra results of fly ash: (a) Tested locations from Mg1, corresponding to Raman spectra of (c); Tested locations from Mg2, corresponding to Raman spectra of (d); (e) XRD results of mullite-quartz phase in Mg1 and Mg2.

Table 2. Assignments of the Raman bands obtained in the studied particles

Fly ash

Particles	Wavenumber (cm ⁻¹)	Assignment	Particles	Wavenumber (cm ⁻¹)	Assignment
1-1	468	Si-O(sym.bend)	2-1	326, 727	Al-O(bend)、Al-O-Si
	333	Al-O(bend)		467	Si-O(sym.bend)
	781	Al-O-Si	2-2	1344, 1582	Amorphous carbon
1-2	471, 897	Si-O(sym.bend and sym.str)	2-3	909	Si-O (sym.str)
			1-3	471	Si-O(sym.bend)
211	Al-O(bend)	467		Si-O(sym.bend)	
1-4	468	Si-O(bend)	2-4	766	Al-O-Si
Mullite-Quartz Phase					
Particles	Wavenumber (cm ⁻¹)	Assignment	Particles	Wavenumber (cm ⁻¹)	Assignment
f1-1	279, 935	Al-O(bend and sym.str)	f2-1	1344, 1590	Amorphous carbon
f1-2	469	Si-O(bend)	f2-2	462	Si-O(bend)
f1-3	468	Si-O(sym.bend)	f2-3	336, 742	Al-O(bend and sym.str)
	764	Al-O(sym.str)		477	Si-O(sym.bend)
Iron-Rich Microsphere Phase					
Particles	Wavenumber (cm ⁻¹)	Assignment	Particles	Wavenumber (cm ⁻¹)	Assignment
g1-1	225, 286	Fe-O(sym.str and sym.bend)	g2-1	267, 410, 481,	—
				614, 662	—
g1-2	468	Si-O(bend)	g2-2	1003, 1107	—
	206, 264	Al-O(bend)		468	Si-O(sym.bend)
	473	Si-O(sym.bend)		910	Si-O(asym. str)
g1-3	665	Maghemite (sym. str)	g2-3	473	Si-O(bend)
g1-4	470	Si-O(sym.bend)	—	—	—

note: (sym.str), (asym. str), (sym.bend) and (bend) stand for symmetric tensile vibration, asymmetric tensile vibration, symmetric bending vibration and bending vibration mode, respectively.

4. Conclusions

This study employed micro-Raman spectroscopy in conjunction with other advanced analytical methods such as XRF, XRD, and FT-IR to analyze the mineral composition of fly ash. The results

indicate that the primary chemical constituents of fly ash were primarily composed of SiO_2 , Al_2O_3 , and Fe_2O_3 , with the dominant crystalline minerals being mullite and quartz, which contained aluminosilicate and silicate components, respectively. Micro-Raman spectroscopy analysis of the isolated mineral phases revealed minerals that were challenging to identify in raw fly ash samples. Specifically, it identified hematite, magnetite and glass within the iron-rich microsphere phase, as well as organic carbon components within the mullite-quartz phase. Furthermore, the confirmation of mullite and quartz as the crystalline minerals present in the mullite-quartz phase underscores the accuracy of the analysis. These findings underscore the capability of micro-Raman spectroscopy in efficiently analyzing glass phase structures and other phases, with its high-resolution chemical mapping and the confocal microscopic imaging properties are crucial for reliably characterizing the mineralogical properties of fly ash.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Response Letter

Dear editors and reviewers,

The authors thank the reviewers for their valuable comments that help improve the paper. Each comment/suggestion from the reviewers has been put in italics and is followed by response and/or explanation of revision accordingly. The modifications to the manuscript with respect to the reviewers' comments are highlighted using different colors.

REVIEWER(R)

Comment 1:

There are some format problems in the article, for example, the first sentence of each paragraph is not indented by two characters, please the author carefully check and modify.

Reply 1:

Thank you for your careful suggestion. Manuscript formats have been reviewed and adjusted to make them more standardized.

Comment 2:

In the 3.2 part, X-ray diffraction technology has been used to confirm the existence of silicate crystals in fly ash, while the 3.3 part also only proves the existence of silicate crystals in fly ash, so is the 3.3 part still necessary?

Reply 2:

Thank you for your insightful question. Although the existence of silicate crystals in fly ash was found by X-ray diffraction technology in 3.2, it is difficult to analyze them at the level of single particles and accurately analyze the composition of amorphous phase. However, microscopic Raman technology can observe the morphology of single particles of fly ash through microscopic imaging technology and obtain the composition of particles at the same time. Therefore, through the micro-Raman analysis of fly ash and its mineral phases in part 3.3, the composition of fly ash particles in different forms can be obtained, and it is found that fly ash particles not only include silicate crystals, which enhances the breadth and credibility of fly ash composition analysis.

Comment 3:

In the analysis of the results, the author cited a large number of previous research results to explain his own

experimental phenomena, and whether the experimental conditions and sample characteristics of the predecessors are different from the samples used by the author, and whether the author has discussed the rationality of the explanation ?

Reply 3:

Thank you for your insightful question. Although the experimental sample used in this paper is different from the fly ash sample used by predecessors, the composition and structure of the fly ash sample in this study are found to be similar to those in other studies through XRD, XRF and FT-IR analysis. Therefore, the article can be cited to explain this paper. Details of this discussion are presented in **Sections 3.1, 3.2, and 3.3**.

Comment 4:

The author has used many advanced technologies to analyze the mineral composition of fly ash, so has the author thought about the reuse of fly ash ?

Reply 4:

Thank you for your careful suggestion. This paper uses these advanced technologies to analyze the composition of fly ash and its mineral phase, which can lay a foundation for the reuse of fly ash. In the future, the author will focus on the reuse of fly ash in various fields.

REVIEWER(M)

Comment 1:

In Section 2.2, the removal of amorphous silicates from ash is worth examining. References are needed to illustrate the feasibility of acid-base combined methodology and isolate the crystalline phase (mullite-quartz phase). As we know, quartz also reacts with NaOH, which leads to the decrease of quartz phase in ash.

Reply 1:

Thank you for your careful suggestion. The acid-base combined method we use is mainly to remove the non-crystalline silicaluminate of fly ash through mild acid-base medium and make use of the difference between the crystalline phase and the amorphous phase reaction activity. The main component of the amorphous phase of fly ash is amorphous silicaluminate, so it can effectively separate the crystalline phase from the amorphous phase. This method is also widely used to dissolve the glass phase of fly ash. Relevant references have been added to **section 2.2** of the paper. At the same time, the presence of quartz was also detected in the XRD analysis of

mullite-quartz phase in section 3.3.2. Therefore, sodium hydroxide mainly reacted with amorphous silica in the combined acid-base leaching process and had little effect on the quartz phase.

Comment 2:

In Section 3.3.2, it is necessary to compare and analyze the Raman spectra of ash before and after acid-base separation, and the change of silicate structure in ash, and the structural characteristics of amorphous silicate.

Reply 2:

Thank you for your insightful question. The Raman spectral characteristic peaks of each structure before and after mineral phase separation are displayed in Table 2, and the characteristic spectral peaks of amorphous aluminosilicate and aluminosilicate crystals are compared, and detailed explanations are presented in section 3.3.3.

Comment 3:

The XRD analysis in manuscript briefly explains the proportion of amorphous amount, and it is suggested that the quantitative analysis of XRD be carried out to further show the proportion of mineral phase and amorphous phase in ash.

Reply 3:

Thank you for your careful suggestion. Due to the complex composition of fly ash, rich phase types, and mainly composed of amorphous phase, crystal phase content is low, can not be quantitative analysis of the crystalline phase by XRD. In this paper, the combined acid-base leaching method can effectively remove the amorphous phase substances in fly ash, so as to obtain a more accurate ratio of crystalline phase to amorphous phase in fly ash. Relevant results are presented in Section 3.3.2.

Comment 4:

In Section 3.3.3, the identification of hydrated ferrous sulfate should be cautious, because this mineral is rare in ash. First of all, the strong hydroxyl peak in the hydrate does not appear in the spectrum. Secondly, I prefer to see the EDS analysis of the mineral to illustrate that it exist in the ash.

Reply 4:

Thank you for your insightful feedback, which has helped us to improve our manuscript. We apologize for

the earlier misidentification of the composition of this particle. We have now corrected this to indicate that this particulate matter is not hydrated ferrous sulfate, and after extensive literature review we do not find a substance corresponding to its Raman characteristic peak, so this particulate matter will not be defined in this paper. Now the relevant content has been modified in [section 3.3](#). Meanwhile, we will conduct in-depth analysis of the composition of this particulate matter in the future work. In addition, SEM-EDS results and analysis of fly ash have been added to [section 3.1](#) of the paper. Thank you again for your timely pointing out the errors in our paper.

ACCEPTED MANUSCRIPT