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RESEARCH ARTICLE

CHEMICAL ANALYSIS OF RAW MATERIALS AND FLY ASH FOR REFRACTORIES

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Abstract. *This study aims to investigate the chemical composition, phase transformations, and microstructural characteristics of natural clay and fly ash from a thermal power plant (TPP) for their combined use in refractory materials, with a focus on compatibility within an aluminosilicate matrix and its influence on material performance. The chemical composition of raw materials was determined using X-ray fluorescence spectroscopy (XRF). Phase composition and high-temperature transformations were analyzed by X-ray diffraction (XRD). Microstructural features, particle morphology, and elemental distribution were examined using scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS). Comparative analysis of major oxides (SiO_2, Al_2O_3, Fe_2O_3, TiO_2) was conducted across all samples. The results show that fly ash consists of fine, predominantly spherical aluminosilicate particles that enhance packing density and reactivity. Its incorporation into the clay matrix promotes intensified mullite formation during heat treatment due to increased availability of reactive silica and alumina. XRD analysis confirmed the formation of primary and secondary mullite phases, while the presence of alkali oxides in fly ash influenced glass phase formation and accelerated phase transformations in the contact zone between clay and ash particles. SEM observations revealed improved microstructural homogeneity and reduced porosity in the modified compositions. The integration of fly ash as a partial substitute for natural clay improves phase development, enhances microstructural properties, and reduces raw material consumption. The findings confirm the potential of utilizing industrial waste in refractory production, contributing to resource-efficient technologies and advancing sustainable practices within green chemistry and industrial ecology.*

Keywords: *refractory clay, TPP ash, chemical composition, X-ray fluorescence analysis, phase composition, fly ash, mullite, X-ray diffraction analysis, aluminosilicate raw materials, waste disposal*

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ҒЫЛЫМИ МАҚАЛА

ОТҚА ТӨЗІМДІ МАТЕРИАЛДАР ӨНДІРІСІНДЕ ҚОЛДАНЫЛАТЫН ШИКІЗАТ ПЕН ҰШПА КҮЛДІҢ ХИМИЯЛЫҚ ТАЛДАУЫ

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Аңдатпа. *Бұл зерттеу табиғи саз бен жылу электр станциясының (ЖЭС) ұшпа күлінің химиялық құрамын, фазалық түрленулерін және микроструктуралық сипаттамаларын зерттеуге, оларды отқа төзімді материалдар өндірісінде бірлесіп қолдану мақсатында, алюмосиликатты матрицадағы үйлесімділігін және оның материал қасиеттеріне әсерін бағалауға бағытталған. Бастапқы материалдардың химиялық құрамы рентгенфлуоресценттік талдау әдісімен анықталды, фазалық құрамы мен жоғары температуралық түрленулері рентгенфазалық талдау арқылы, ал микроструктуралық ерекшеліктері, бөлшектер морфологиясы және элементтердің таралуы сканерлеуші электрондық микроскопия (СЭМ) және энергиядисперсиялық талдау көмегімен зерттелді. Негізгі оксидтердің (SiO_2, Al_2O_3, Fe_2O_3, TiO_2) мөлшеріне салыстырмалы талдау жүргізілді. Зерттеу нәтижелері ұшпа күлдің негізінен ұсақ дисперсті, шар тәрізді алюмосиликат бөлшектерден тұратынын көрсетті, бұл жүйенің тығыздалуын және реакциялық қабілетін арттырады. Күлді сазды матрицаға енгізу термиялық өңдеу кезінде муллит түзілуін күшейтеді, себебі реакцияға қабілетті кремнезем мен глинозем мөлшері артады. Рентгенфазалық талдау бастапқы және екінші реттік муллит фазаларының түзілуін растады, ал күл құрамындағы сілтілі оксидтер шыны фазасының қалыптасуына әсер етіп, саз бен күл бөлшектерінің жанасу аймағында фазалық түрленулерді жеделдетеді. СЭМ талдауы модификацияланған құрамдардың микроструктурасының біркелкілігінің артуын және кеуектіліктің төмендеуін көрсетті. Ұшпа күлді табиғи сазды ішінара алмастыру ретінде қолдану материал қасиеттерін жақсартып, шикізат шығынын азайтады және өндірістік қалдықтарды пайдалану арқылы ресурс үнемдейтін технологияларды дамытуға мүмкіндік береді.*

Түйін сөздер: *отқа төзімді саз, ЖЭО күлі, химиялық құрамы, рентгенфлуоресценттік талдау, фазалық құрамы, ұшпа күл, муллит, рентгенқұрылымдық талдау, алюмосиликатты шикізат, қалдықтарды кәдеге жарату*

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НАУЧНАЯ СТАТЬЯ

ХИМИЧЕСКИЙ АНАЛИЗ СЫРЬЯ И ЛЕТУЧЕЙ ЗОЛЫ ДЛЯ ПРОИЗВОДСТВА ОГНЕУПОРНЫХ МАТЕРИАЛОВ

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Аннотация. *Данное исследование направлено на изучение химического состава, фазовых превращений и микроструктурных характеристик природной глины и летучей золы тепловой электростанции (ТЭС) с целью их совместного использования в производстве огнеупорных материалов, с акцентом на совместимость в алюмосиликатной матрице и её влияние на свойства материала. Химический состав исходных материалов был определен методом рентгенофлуоресцентного анализа, фазовый состав и высокотемпературные превращения — методом рентгенофазового анализа, а микроструктурные особенности, морфология частиц и распределение элементов — с использованием сканирующей электронной микроскопии (СЭМ) в сочетании с энергодисперсионным анализом. Проведён сравнительный анализ содержания основных оксидов (SiO_2, Al_2O_3, Fe_2O_3, TiO_2). Результаты показали, что летучая зола состоит из тонкодисперсных преимущественно сферических алюмосиликатных частиц, повышающих плотность упаковки и реакционную способность системы. Введение золы в глинистую матрицу способствует интенсификации образования муллита при термической обработке за счёт увеличения содержания реакционноспособных форм кремнезёма и глинозёма. Рентгенофазовый анализ подтвердил образование первичных и вторичных фаз муллита, а присутствие щелочных оксидов в золе влияет на формирование стеклофазы и ускоряет фазовые превращения в контактной зоне между частицами глины и золы. СЭМ-анализ показал улучшение однородности микроструктуры и снижение пористости модифицированных составов. Использование летучей золы как частичной замены природной глины способствует улучшению свойств материала и снижению расхода сырья, подтверждая перспективность применения промышленных отходов в рамках ресурсосберегающих технологий и принципов «зелёной» химии.*

Ключевые слова: *огнеупорная глина, зола ТЭЦ, химический состав, рентгенофлуоресцентный анализ, фазовый состав, зола-унос, муллит, рентгеноструктурный анализ, алюмосиликатное сырье, утилизация отходов*

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CONFLICT OF INTEREST

The authors state that there is no conflict of interest.

During the preparation of this manuscript, the authors used artificial intelligence tools (ChatGPT) solely for editorial assistance, such as improving phrasing and checking grammar, spelling, and punctuation. All ideas, interpretations, and conclusions are the responsibility of the authors, who take full accountability for the content of the article.

АЛҒЫС / ҚАРЖЫЛАНДЫРУ КӨЗІ

Зерттеу Қазақстан Республикасы Ғылым және жоғары білім министрлігі Ғылым комитетінің AP26193815 "Энергетика кәсіпорындарының қалдықтарын пайдалана отырып, отқа төзімді материалдар технологиясының ғылыми-техникалық негіздерін әзірлеу" гранттық қаржыландыру шеңберінде жүргізілді..

МҮДДЕЛЕР ҚАҚТЫҒЫСЫ

Авторлар мүдделер қақтығысы жоқ деп мәлімдейді.

Мақаланы дайындау барысында авторлар жасанды интеллект құралдарын (ChatGPT) тек редакциялық көмек мақсатында пайдаланды: тұжырымдарды жетілдіру, грамматикалық, орфографиялық және тыныс белгілеріндегі қателерді тексеру үшін. Барлық идеялар, интерпретациялар мен қорытындылар авторларға тиесілі, және олар мақаланың мазмұнына толық жауапты

БЛАГОДАРНОСТИ/ИСТОЧНИК ФИНАНСИРОВАНИЯ

Исследование проводилось в рамках грантового финансирования Комитета науки Министерства науки и высшего образования Республики Казахстан AP26193815 “Разработка научно-технических основ технологии огнеупорных материалов с использованием отходов предприятий энергетики”.

КОНФЛИКТ ИНТЕРЕСОВ

Авторы заявляют, что конфликта интересов нет.

При подготовке рукописи авторы использовали инструменты искусственного интеллекта (ChatGPT) исключительно для редакторской поддержки: корректировки формулировок, проверки грамматических, орфографических и пунктуационных ошибок. Все идеи, интерпретации и выводы принадлежат авторам, которые несут полную ответственность за содержание статьи.

1 INTRODUCTION

The modern construction and refractory materials industry is increasingly confronted with the need to transform its raw material base in response to resource depletion and environmental challenges. The extensive use of high-quality natural clays leads to their gradual exhaustion and rising extraction and transportation costs. At the same time, the global energy sector generates significant volumes of fly ash as a by-product of coal combustion at thermal power plants, posing serious environmental risks associated with ash disposal, including soil and groundwater contamination by toxic elements. In the context of the circular economy and sustainable materials science, the valorization of technogenic raw materials, such as fly ash, into high-performance refractory materials represents a promising research direction **(Kamara et al. 2020)**.

Recent studies indexed in Scopus and Web of Science emphasize the growing interest in the reuse of industrial by-products for advanced ceramic applications, particularly in the development of eco-efficient and resource-saving technologies. However, while the incorporation of fly ash has been widely investigated in building ceramics and cement systems, its application in refractory materials remains relatively limited due to stricter requirements for thermal stability, chemical purity, and phase composition. In particular, the role of impurity oxides (Fe_2O_3, TiO_2, CaO) and alkaline components in phase transformations and high-temperature behavior is not sufficiently understood **(Valášková et al. 2021)**.

Clay and fly ash represent complex multicomponent aluminosilicate systems with comparable chemical compositions characterized by high contents of SiO_2 and Al_2O_3. This similarity creates favorable conditions for their combined thermal processing and the potential formation of high-temperature phases such as mullite. Nevertheless, the variability of ash composition, depending on coal type and combustion conditions, introduces significant uncertainty in predicting phase evolution and material performance. In addition, the kinetics of mullite formation in the presence of ash microspheres and the influence of glass-forming components on the structure of the ceramic matrix require further investigation **(Pregernik et al. 2025)**.

The modern paradigm of building materials science and refractory technologies is increasingly oriented toward the utilization of secondary and technogenic raw materials due to the depletion of high-quality natural aluminosilicates and growing environmental constraints. In this context, fly ash from thermal power plants (TPPs) is widely considered a promising resource with a complex phase composition consisting of both glassy and crystalline components **(Koshy et al. 2021)**. Its incorporation into clay matrices has been shown to significantly alter phase transformation pathways during thermal treatment.

A number of studies have focused on the interaction between kaolinite ($Al_2Si_2O_5(OH)_4$), the main component of refractory clays, and aluminosilicate glass present in fly ash. It has been established that at temperatures above 1100 °C, the clay structure undergoes decomposition, leading to the formation of reactive silica, which interacts with alumina from ash to form secondary mullite **(Khater et al. 2024; Das et al. 2020)**. The needle-like morphology of mullite is widely recognized as a key factor enhancing the thermal stability and mechanical strength of refractory materials. However, most of these studies are conducted under controlled laboratory conditions and do not sufficiently account for the variability in ash composition, which limits their applicability in industrial practice.

Considerable attention has also been given to the role of impurity oxides such as Fe_2O_3, TiO_2, CaO, and alkali oxides (K_2O, Na_2O), whose concentrations in fly ash can vary significantly depending on fuel type and combustion conditions **(Wang et al. 2020)**. These components exhibit a dual effect: on one hand, they can act as mineralizers that promote mullite formation **(Tabit et al. 2020)**, while on the other hand, they contribute to the formation of low-melting glassy phases that reduce refractoriness **(Hossain et al. 2020; Agarwal et al. 2020)**. Despite the availability of such studies, a systematic understanding of the balance between these competing effects remains limited.

Microstructural investigations using scanning electron microscopy reveal that fly ash particles typically exhibit a spherical morphology (cenospheres and plerospheres), which improves workability and reduces the viscosity of clay mixtures **(Chen et al. 2020; Bhatt et al. 2019)**. Nevertheless, as highlighted by **Ma et al. (2019)** and **Abildaeva et al. (2022)**, improper control of particle size distribution may lead to increased porosity and reduced density, negatively affecting the performance of refractory materials. This underscores the need for precise control of structural parameters.

From an environmental and economic perspective, the utilization of fly ash is often discussed within the framework of industrial symbiosis, where waste streams are re-integrated into production cycles **(Fu et al. 2019; Li et al. 2019)**. Furthermore, recent studies indicate that eutectic melts formed in ash-containing systems can reduce sintering temperatures and energy consumption **(Maikonov et al. 2025; Takirova et al. 2025)**. However, the majority of these studies are focused on construction ceramics, where performance requirements are less stringent compared to refractory materials **(Ibrayeva et al. 2025; Kultayeva 2025)**.

Thus, the analysis of the literature indicates that existing research is predominantly focused on the use of fly ash in building materials and does not fully address the specific requirements of refractory systems. The main research gap lies in the insufficient understanding of the combined influence of ash chemical composition, particularly impurity oxides, on phase formation, mullite formation kinetics, and microstructural evolution in clay–ash systems under high-temperature conditions. In addition, there is a lack of comprehensive comparative studies of natural and technogenic raw materials from the perspective of their joint application in high-temperature refractory compositions.

Addressing this gap requires an integrated approach combining chemical, phase, and microstructural analysis, which defines the scope and direction of the present study.

The scientific novelty of this study lies in the comprehensive assessment of the interaction between natural refractory clay and fly ash with varying oxide compositions, with a particular focus on impurity effects on phase formation and high-temperature behavior. Unlike existing studies, which are primarily oriented toward construction materials, this work addresses the application of technogenic components in refractory systems operating under extreme thermal conditions.

The aim of this study is to conduct a comparative analysis of the chemical composition of natural refractory clay and fly ash, as well as to investigate their interaction during high-temperature synthesis.

To achieve this aim, the following research objectives are defined:

- to determine the concentration of major and impurity oxides using X-ray fluorescence (XRF) analysis;
- to identify phase transformations and crystalline structure evolution using X-ray diffraction (XRD);
- to analyze the microstructure of the obtained materials using scanning electron microscopy (SEM);
- to evaluate the potential of fly ash as a component of refractory compositions.

The results of this study provide an analytical basis for the development of new refractory materials with an increased content of technogenic raw materials and improved performance characteristics.

2 MATERIALS AND METHODS

Refractory clay of kaolinite type and fly ash obtained from the dry ash removal system of a coal-fired thermal power plant were used as the primary raw materials. The clay is characterized by high plasticity and stable aluminosilicate composition, while the fly ash represents a heterogeneous aluminosilicate system with variable oxide content.

Prior to analysis, all raw materials were subjected to standardized pre-treatment to ensure reproducibility. Samples were dried at 105–110 °C to constant mass (24 h), followed by mechanical grinding in a planetary mill. The powders were sieved to obtain a particle size fraction below 0.071 mm.

The bulk chemical composition was determined using wavelength-dispersive X-ray fluorescence spectroscopy (WDXRF) on a PANalytical Axios spectrometer. Powder samples were pressed into pellets on a boron substrate under a pressure of 200 kN.

The quantitative analysis included the determination of major and impurity oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, TiO_2). The measurement accuracy was controlled by calibration standards, with a relative standard deviation not exceeding 0.5% for major components.

The phase composition of the raw materials and synthesized samples was analyzed using X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å).

The scanning parameters were as follows:

- angular range (2θ): 5°–80°
- step size: 0.02°
- scan speed: 1–2°/min

Phase identification was performed using the ICDD PDF-2 database. Semi-quantitative phase analysis was carried out based on peak intensity ratios.

The morphology of fly ash particles and the microstructure of sintered samples were investigated using scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS) system.

The analysis was conducted under the following conditions:

- accelerating voltage: 15–20 kV
- working distance: 8–10 mm
- magnification range: ×100–×5000

EDS microanalysis was used to determine the local chemical composition and distribution of elements in the microstructure.

To investigate the interaction between clay and fly ash, model mixtures with varying mass ratios were prepared: 90:10, 80:20, 70:30, 60:40, and 50:50 (clay:ash).

The preparation procedure included:

1. Dry homogenization of components for 10–15 min;
2. Addition of distilled water to achieve a moisture content of 8–10%;
3. Uniaxial pressing into cylindrical specimens (diameter 20–30 mm) under a pressure of 15–20 MPa.

Firing was carried out in a laboratory muffle furnace under controlled conditions:

- temperature range: 1100–1400 °C
- heating rate: 5–10 °C/min
- soaking time at maximum temperature: 2 h
- cooling: furnace cooling to room temperature

These parameters were selected to simulate industrial conditions of refractory material synthesis.

3 RESULTS AND DISCUSSION

The results of X-ray fluorescence analysis (XRF) presented in **Table 1** allow us to assess the potential for using TPP ash as a modifier of clay charge.

Table 1 – Chemical composition of the materials studied (mass %)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O+Na_2O	TiO_2	MgO	LDC*
Refractory clay	53,6	33,4	1,3	0,5	1,0	0,9	0,6	8,2
Fly ash from thermal power plants	56,2	25,8	4,6	2,2	2,3	1,3	0,7	3,4

** LDC - Losses during calcination.*

As presented in **Table 1** the chemical composition analysis indicates that both materials belong to aluminosilicate systems with high contents of SiO_2 and Al_2O_3, suggesting their potential compatibility during high-temperature processing. However, refractory clay is characterized by a higher Al_2O_3 content (33,4 wt.%), which promotes the formation of thermally stable phases, primarily mullite, and contributes to enhanced refractoriness.

In contrast, fly ash exhibits elevated levels of Fe_2O_3 (4,6 wt.%), CaO (2,2 wt.%), and alkali oxides ($K_2O + Na_2O = 2,3$ wt.%), which act as fluxing agents. These components facilitate liquid-phase sintering and reduce the firing temperature, thereby accelerating phase transformations. At the same time, their presence may promote the formation of low-melting glassy phases, potentially limiting the high-temperature performance of the material.

A significant difference is also observed in the loss on ignition (LOI) values: refractory clay shows a higher LOI (8,2 wt.%), associated with the dehydroxylation of kaolinite, whereas fly ash exhibits a lower value (3,4 wt.%), reflecting its prior thermal exposure during coal combustion.

Overall, the combination of alumina-rich clay and flux-containing fly ash creates favorable conditions for controlled sintering and phase evolution. However, optimization of the composition is required to balance densification and refractoriness, minimizing excessive glass formation and preserving high-temperature stability. **Table 2** presents the elemental composition of the studied materials

Table 2 - Elemental composition of the studied materials (mass %, calculated)

Material	Si	Al	Fe	Ca	K+Na*	Ti	Mg
Refractory clay	24,5	18,4	0,84	0,43	0,88	0,54	0,24
Fly ash thermal power plants	27,4	13,9	3,35	1,50	2,00	0,72	0,48

According to **Table 1** the elemental composition further confirms the fundamental differences in the physicochemical behavior of refractory clay and fly ash during high-temperature processing. Refractory clay is characterized by a relatively balanced Si–Al ratio, with significant aluminum content (18,4 wt.% Al), which is favorable for mullite formation and contributes to the development of a stable crystalline framework under elevated temperatures.

In contrast, fly ash exhibits a higher silicon content (27,4 wt.% Si) combined with a noticeably lower aluminum concentration (13,9 wt.% Al), indicating a silica-rich composition that may limit the extent of mullite formation and promote the presence of a residual glassy phase. This imbalance in the Si/Al ratio suggests a shift in phase evolution mechanisms toward increased glass formation during sintering.

A pronounced difference is observed in the concentration of impurity elements. Fly ash contains significantly higher levels of Fe (3,35 wt.%), Ca (1,50 wt.%), and alkali elements (K + Na = 2,00 wt.%), which act as fluxing agents and contribute to liquid-phase formation at lower temperatures. While this can enhance densification and accelerate sintering kinetics, it may also lead to the formation of low-viscosity melts, increasing the risk of structural deformation under high-temperature conditions.

Additionally, the higher content of Ti (0,72 wt.%) and Mg (0,48 wt.%) in fly ash may influence phase stability and crystal growth behavior. These elements can act as modifiers of the crystalline structure, affecting grain growth and potentially contributing to the stabilization of secondary phases.

Overall, the results indicate that refractory clay provides a structurally stable aluminosilicate framework, whereas fly ash introduces reactive and fluxing components that significantly alter the sintering behavior and phase transformation pathways. This combination creates opportunities for tailoring material properties but requires careful compositional control to balance densification, phase formation, and high-temperature performance.

Figure 1 presents a comparative analysis of the elemental composition of fly ash and clay.

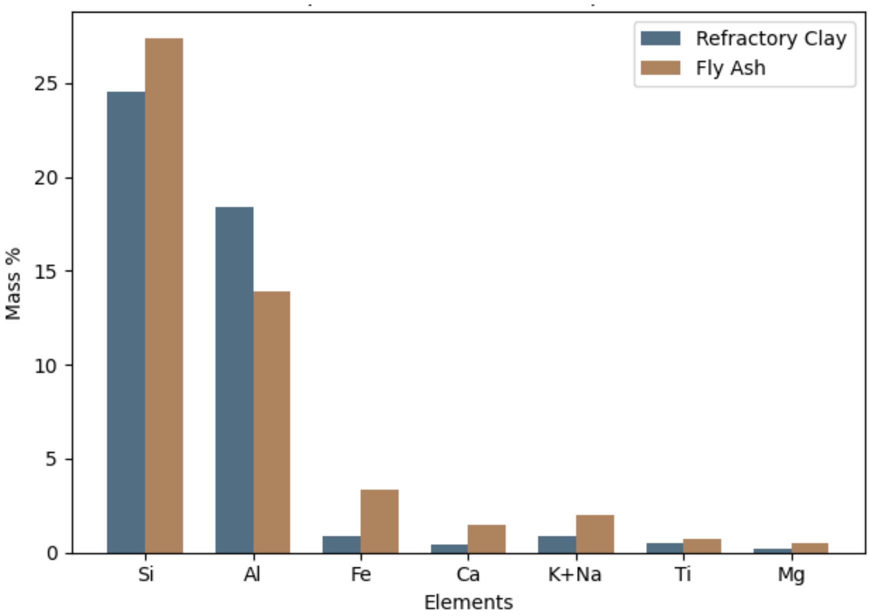

Figure 1 – Comparative analysis of the elemental composition of fly ash and clay (author's materials)

As shown in Figure 1 a comparison of the mass fractions of the main chemical elements in refractory clay and ash fly ash from a thermal power plant, calculated based on X-ray fluorescence analysis data.

Analysis of the distribution of elements reveals the following patterns:

The silicon content in ash is higher (27.4%) than in clay (24.5%), which confirms its pronounced siliceous nature and potential ability to participate in the formation of aluminosilicate phases.

Refractory clay has a higher aluminum content (18.4%) than ash (13.9%), which gives it greater refractoriness and the ability to form a mullite structure during firing.

The ash is characterized by a significantly higher iron content (3.35% compared to 0.84%), which may influence the color of the products, phase transformations, and sintering behavior.

The elevated calcium content in the ash (1.50%) indicates its fluxing activity and ability to reduce the temperature at which the liquid phase forms.

The content of alkaline elements (K + Na) in ash reaches 2.0%, which is almost 2.3 times higher than in clay. Alkaline oxides are active fluxes that accelerate diffusion processes and sintering during heat treatment.

The titanium (Ti) and magnesium (Mg) content in the ash is also slightly higher, which may contribute to the formation of additional secondary phases under high-temperature exposure.

According to the results of X-ray fluorescence analysis, the ash-carrier from the thermal power plant under investigation does not contain toxic and environmentally hazardous elements in concentrations exceeding the maximum permissible values established by the technical regulations of the Eurasian Economic Union (EAEU), including in terms of the safety of building materials and raw materials.

The content of heavy metals and potentially hazardous impurities is within regulatory limits, which complies with industrial, sanitary, hygienic, and environmental safety requirements.

Thus, the ash under investigation can be considered a safe man-made aluminosilicate material suitable for use in the production of refractory products without restrictions on chemical safety indicators.

Analysis of X-ray diffraction (XRD) data revealed complex transformation dynamics. In its initial state, the clay consists of kaolinite, which transforms into metakaolinite when heated above 550 °C. When fly ash containing a significant amount of amorphous glass phase is added, the sintering process intensifies.

A critically important process, mullitization, occurs in the temperature range of 1150–1350°C. The interaction between the active silica in clay and the aluminum oxide in ash proceeds according to the following stoichiometric **equation (1)**:

$$3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 \quad (1)$$

Here, metakaolinite decomposes to form primary mullite and free SiO_2. The presence of TPP ash introduces additional Al_2O_3 into the system, which reacts with free silica, initiating the growth of secondary mullite. This is confirmed by an increase in the intensity of diffraction maxima at angles 2θ= 16.4°, 26.2°, 33.2°. **Figure 2** presents the phase composition of fly ash from a thermal power plant.

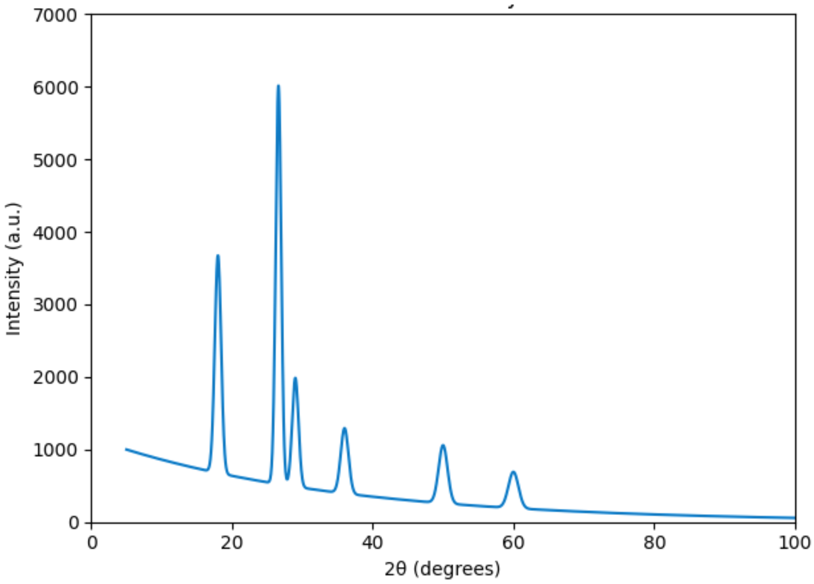

Figure 2 - Phase composition of fly ash from a thermal power plant (author’s materials)

As shown in Figure 2 the diffractogram of fly ash obtained by X-ray phase analysis (CuKα radiation) is presented in the angle range 2θ = 5–100°. The abscissa axis shows the diffraction angle 2θ (degrees), while the ordinate axis shows the intensity of the diffraction signal (relative units).

Analysis of the diffractogram shows the presence of a pronounced diffuse maximum in the 15–30° 2θ range, indicating a significant proportion of amorphous glassy phase. The presence of an amorphous component is characteristic of fly ash formed during rapid cooling of molten mineral components of coal.

The most intense crystalline reflection was recorded at 2θ ≈ 26.6°, which corresponds to quartz (SiO_2). Additional peaks in the regions of 20°, 29–30°, 36°, 50°, and 60° 2θ may be associated with aluminosilicate and iron-containing phases.

Thus, fly ash is characterized by a mixed amorphous-crystalline structure with a predominance of quartz and a glassy aluminosilicate matrix, which determines its potential reactivity during heat treatment and interaction with mineral components of the charge. **Figure 3** presents the phase composition of refractory clay.

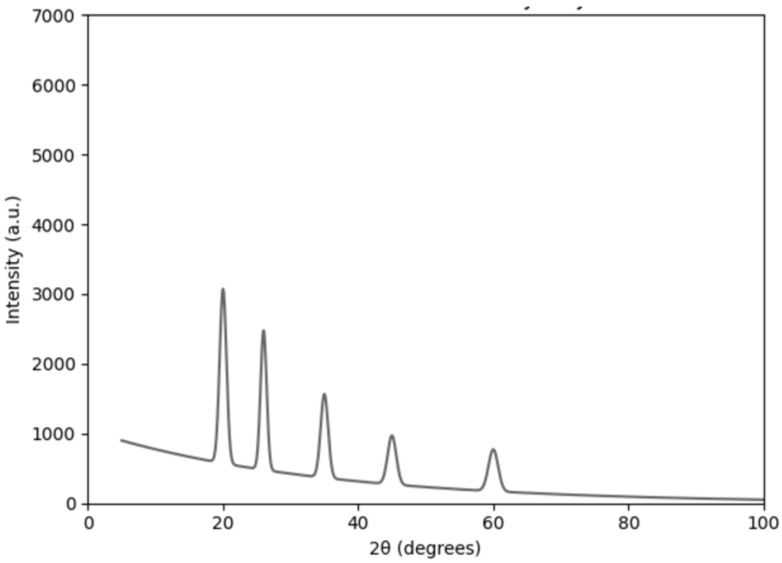

Figure 3 - Phase composition of refractory clay (author's materials)

As shown in Figure 3 the diffractogram of refractory clay was also recorded in the range of 2θ = 5–100°. Unlike ash, the structure of clay is characterized by more pronounced crystalline peaks and a less intense amorphous background.

The main diffraction peaks are observed at:

- 2θ ≈ 20–21°;
- 2θ ≈ 26°;
- 2θ ≈ 35°;
- 2θ ≈ 45°;
- 2θ ≈ 60°.

The peak at 2θ ≈ 26° corresponds to quartz. Reflections in the range of 20–25° 2θ may be due to the presence of clay minerals (kaolinitic or hydromica nature). Higher intensity and sharpness of peaks indicate a higher degree of crystallinity compared to fly ash.

Comparison of the diffractograms shows:

- fly ash contains a significant proportion of amorphous glassy phase;
- refractory clay is characterized mainly by a crystalline structure;
- quartz is the main crystalline phase in both materials;
- higher amorphousness of ash causes its increased reactivity.

The data obtained confirm the feasibility of using fly ash as a modifying additive to clay charge, since the amorphous aluminosilicate component is capable of participating in phase formation processes during heat treatment and contributing to the intensification of sintering.

To evaluate the influence of composition and firing temperature on the microstructure and sintering behavior of clay–ash systems, scanning electron microscopy (SEM) analysis was performed. Particular attention was paid to the effect of fly ash content on densification, pore structure, and phase interaction during heat treatment.

Figure 4 shows micrographs of samples with different clay:ash ratios (90:10 and 50:50), obtained by scanning electron microscopy after heat treatment at 1100 and 1400 °C.

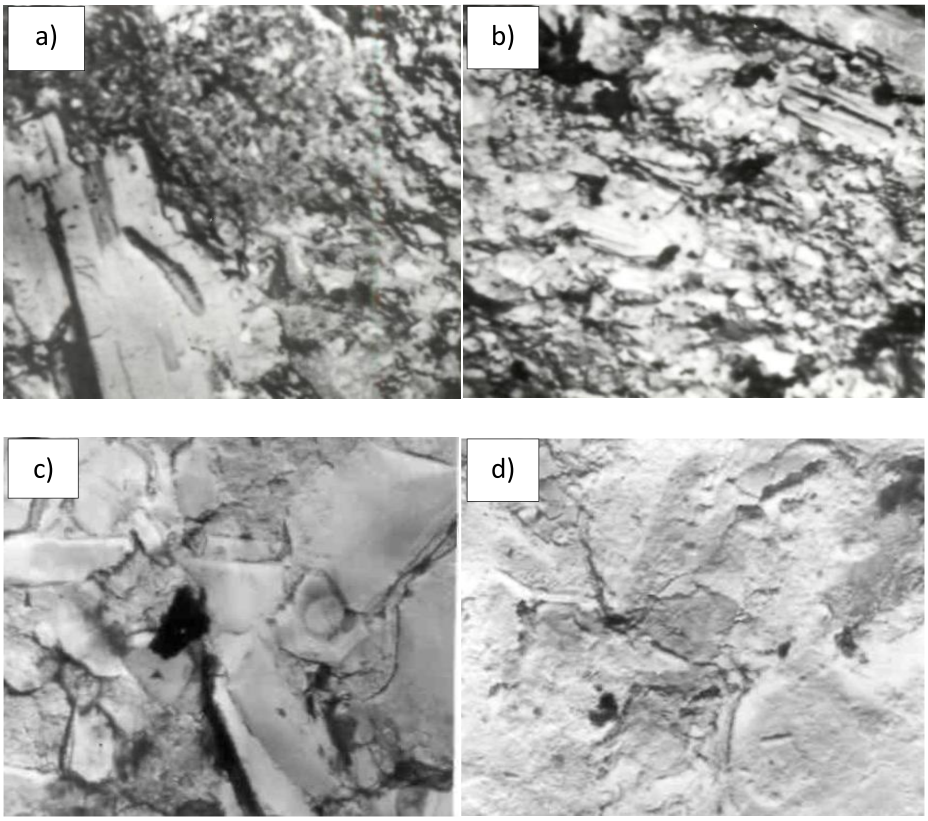

Figure 4 - Microstructure of clay-ash samples after firing at 1100 and 1400 °C (SEM): a) 90:10, 1100 °C; b) 90:10, 1400 °C; c) 50:50, 1100 °C; d) 50:50, 1400 °C (author's materials)

As shown in Figure 4a, the microstructure of the sample with a clay:ash ratio of 90:10 after firing at 1100 °C is characterized by a relatively loose structure with developed porosity and insufficient sintering. The particles largely retain their original morphology, indicating a low degree of interaction between the components. Pronounced intergranular voids and a limited number of contact zones are observed, which suggests that the formation of a continuous binding phase has not yet occurred. This microstructural state corresponds to an early stage of sintering, where particle rearrangement dominates over diffusion-controlled densification processes.

As illustrated in Figure 4b, increasing the firing temperature to 1400 °C leads to a significant enhancement of sintering. The structure becomes denser and more homogeneous, with a noticeable reduction in open porosity. The number of interparticle contacts increases, and partial coalescence of grains is observed, indicating the development of a glassy phase and the onset of liquid-phase sintering.

According to Figure 4c, the sample with a higher ash content (50:50) fired at 1100 °C exhibits a more heterogeneous structure compared to the 90:10 composition. The presence of fine ash particles contributes to partial filling of pores; however, the overall degree of sintering remains limited. The structure still contains significant porosity, although a greater number of nucleation sites for phase formation can be identified.

As shown in Figure 4d, at 1400 °C the 50:50 composition demonstrates the most pronounced densification effect. The microstructure becomes significantly more compact, with reduced pore size and improved homogeneity. This is attributed to the higher content of amorphous aluminosilicate phase introduced with fly ash, which promotes liquid-phase formation, enhances diffusion processes, and intensifies mullite crystallization.

Microstructural analysis showed that the following changes occur as the firing temperature increases:

- compaction of the structure and reduction of open porosity;
- formation of contact zones between ash and clay particles;

- the appearance of liquid phase sintering areas;
- formation of secondary aluminosilicate phases.

In compositions with an ash content of 10–30%, the structure is characterized by a more uniform distribution of pores and the formation of a dense matrix. The amorphous component of ash is actively involved in phase formation processes, contributing to the formation of an additional binding phase.

When the ash content increases to 40–50%, there is an increase in the amount of the glassy phase and intensification of liquid-phase sintering, which leads to a decrease in porosity. However, if the content of fluxing components is excessive, an excess glassy matrix may form.

The microstructural data obtained indicate that ash carryover performs a dual function:

1. as a reactive aluminosilicate component;
2. as a fluxing additive that activates sintering processes.

The optimal ratio of components ensures the formation of a dense, homogeneous structure with developed intergranular bonding, which directly affects the performance characteristics of the resulting refractory materials.

4 CONCLUSIONS

A comprehensive study of the chemical, phase, and microstructural characteristics of the “refractory clay – TPP fly ash” system has yielded the following key conclusions:

1. X-ray fluorescence analysis revealed that the investigated fly ash is an aluminosilicate material with a high content of SiO_2 (≈56.2 wt.%) and Al_2O_3 (≈25.8 wt.%). The total content of acidic oxides ($SiO_2 + Al_2O_3 + Fe_2O_3 > 80$ wt.%) confirms its suitability as a technogenic substitute for natural clay raw materials in medium-alumina refractory production. The elevated Fe_2O_3 content (3.35%) compared to clay (0.84%) may additionally influence phase evolution and sintering behavior.

2. X-ray diffraction analysis demonstrated that fly ash exhibits a mixed amorphous–crystalline structure dominated by quartz and a significant proportion of reactive amorphous aluminosilicate phase, whereas the clay is predominantly crystalline. The presence of up to ~40–60% amorphous phase in ash enhances its reactivity, promoting intensified mullite formation and accelerating phase transformations during thermal treatment.

3. SEM analysis confirmed that the incorporation of fly ash leads to improved packing density and microstructural homogeneity. At firing temperatures of 1100–1400 °C, the formation of an additional glassy bonding phase reduces porosity and enhances densification, resulting in a more uniform and compact structure.

The study establishes the relationship between chemical composition, amorphous phase content, and sintering behavior in aluminosilicate systems modified with fly ash. It provides new insights into the role of technogenic aluminosilicates in mullite formation and microstructural evolution of refractory materials.

The results justify the use of TPP fly ash as a partial replacement (up to 20–50%) for natural clay, enabling:

- reduction of raw material consumption;
- improvement of material properties (density, homogeneity);
- reduction of environmental impact through ash utilization.

Thus, the demonstrated chemical compatibility and phase synergy of natural clay and fly ash confirm the feasibility of implementing these compositions in refractory production. Further research should focus on optimizing particle size distribution and its effect on porosity and gas permeability.

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