

Research Article

Bakhtiyar Sadykov, Ainur Khairullina, Aida Artykbayeva, Alua Maten, Anar Zhapekova, Aigul Turesheva and Ayagoz Bakkara*

Development of optimal modes of mechanochemical treatment of technogenic raw materials with various modifiers to produce heat-insulating materials

<https://doi.org/10.1515/pac-2025-0581>

Received August 7, 2025; accepted October 9, 2025

Abstract: This paper presents the results of studies on the effect of mechanochemical treatment (MCT) and modification of technogenic waste based on ash and fly ash. Mechanical modification was carried out using a laboratory ball mill with the addition of organic modifiers to the system. After MCT, the physicochemical properties of the obtained modified ash and fly ash particles were studied. Heat insulators based on ash and slag after MCT have a noticeable positive effect on its rheological properties, improving its structure and heat resistance. Self-propagating high-temperature synthesis (SHS) samples with fly ash after MCT showed a significant decrease in thermal conductivity, which leads to improved heat-insulating properties. The obtained samples based on technogenic waste are effective heat-resistant and environmentally friendly materials that are superior to many traditional analogues.

Keywords: heat-insulating materials; mechanochemical treatment; modification; self-propagating high-temperature synthesis; technogenic raw materials.

Introduction

With the ongoing socio-economic development, improving the energy efficiency of buildings has become an increasingly important focus, where enhancing the thermal insulation performance of building envelopes is considered a key strategic objective. At the same time, the incorporation of solid industrial waste into insulation materials has gained significant attention as a viable solution that supports both material resource optimization and environmental sustainability within the construction sector.^{1–4}

When producing high-temperature heat insulators, the range of used initial mineral compounds is expanded. Both natural and man-made raw materials can serve as initial components. Analysis of new special materials for heat and thermal protection shows that when developing these materials, it is necessary to use unused or little-used industrial waste with heat-insulating properties, which will allow for a comprehensive solution to technical, economic and environmental problems.^{5–7}

*Corresponding author: **Ayagoz Bakkara**, The Institute of Combustion Problems, Almaty, Republic of Kazakhstan; and Farabi University, Almaty, Republic of Kazakhstan, e-mail: bakkara.ayagoz@kaznu.kz. <https://orcid.org/0000-0001-7336-126X>

Bakhtiyar Sadykov, Ainur Khairullina and Aigul Turesheva, The Institute of Combustion Problems, Almaty, Republic of Kazakhstan

Aida Artykbayeva and Alua Maten, The Institute of Combustion Problems, Almaty, Republic of Kazakhstan; and Farabi University, Almaty, Republic of Kazakhstan

Anar Zhapekova, The Institute of Combustion Problems, Almaty, Republic of Kazakhstan; and Kazakh National Women's Teacher Training University, Almaty, Republic of Kazakhstan

In 2022, the 27th United Nations Climate Change Conference focused on key themes such as climate change mitigation, adaptation strategies, climate finance, and multilateral cooperation. The final declaration emphasized that improving resource efficiency is an essential strategy for achieving global climate targets. Against the backdrop of accelerating depletion of natural resources, this approach becomes increasingly critical. In this study, the report “Sustainable Earth and Human Health” is adopted as a conceptual framework to explore pressing issues, including the efficient use of recyclable materials, the reduction of energy consumption, and the creation of a healthy, comfortable, and energy-efficient indoor environment.⁸

Waste from thermal power plants is a promising raw material for obtaining various valuable products and contributes to the development of the construction complex. The main technogenic waste from thermal power plants and state district power plants are ash, fly ash and flue gases. In the Republic of Kazakhstan, the annual output of ash and ash and slag mixtures from coal combustion is about 19 million tons, and more than 300 million tons of waste have accumulated in ash dumps to date. Although the ash is mainly captured by various filters, about 250 million tons of fine aerosols are still released into the atmosphere annually in the form of emissions from thermal power plants.⁹

Mechanochemical treatment (MCT) is also used to activate and modify raw materials, which contributes to a significant change in the dispersion and structure of the surface layer of particles.¹⁰ It is necessary to establish the relationship between structural changes during MCT of powder materials and the thermokinetic characteristics of the subsequent synthesis process, in particular, technological combustion, in order to effectively control structure, phase and pore formation during the synthesis of composite materials.

The aim of the study is to develop a technology for producing thermal insulation materials based on man-made waste and their use as thermal insulators for the construction of external and internal walls of a building.

Materials and methods of research

In this work, technogenic raw materials were used – fly ash and ash from thermal power plants. X-ray phase analysis of the raw materials was carried out. According to the results of X-ray phase analysis, the composition of the ash: $\text{Al}_2(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{9.6}$ -mullite-70 % and SiO_2 -quartz-29.1 %. A small amount of X-ray amorphous phase (unburned carbon) is present (Fig. 1).

The results of X-ray phase analysis of the fly ash showed that the sample is practically a single phase of the compound $\text{Al}_2(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{9.6}$ – mullite. The sample also contains an X-ray amorphous phase (carbon) (Fig. 2).

The main phase of the used technogenic waste is mullite, silicon dioxide and unburned carbon are contained in small quantities. Mechanochemical processing (MCP) of powders was carried out in centrifugal planetary mills (CPM) “NXQM-2A” with a working chamber volume of 500 mm³, platform rotation speed of 650 rpm, acceleration of grinding balls 40 g, energy consumption of 0.75 kW/h. During grinding, the grinding time, the ratio of the powder mass to the mass of balls (MP/Msh) and the amount of modifying additives introduced were varied. Man-

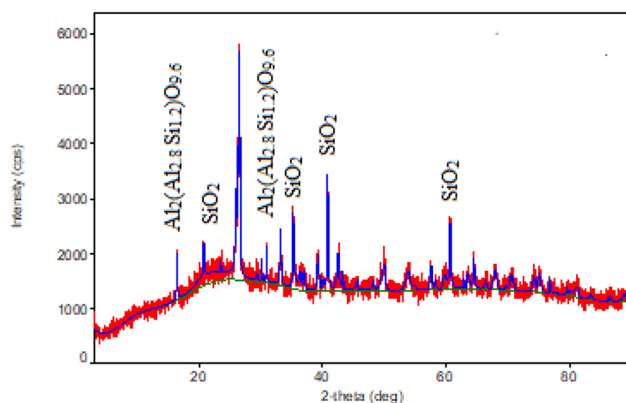


Fig. 1: Diffraction pattern of the initial ash and slag particles.

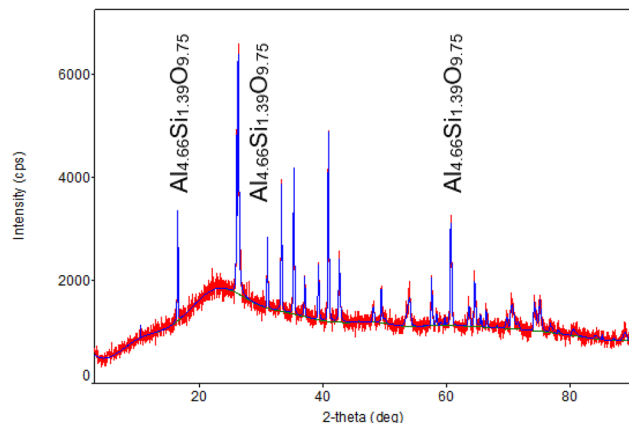


Fig. 2: Diffraction pattern of the initial fly ash particles.

made waste was subjected to grinding in a planetary centrifugal mill for 10, 20, 30 and 40 min at different ratios of powder mass (M_P) and ball mass (M_B), namely at $M_P/M_B = 1/2, 1/3$ and $1/4$. Modifiers were also added – graphite (C), stearic acid (SA) and polyvinyl alcohol (PVA).

SHS compositions of activated and modified powders of ash and fly ash with aluminum were prepared using a hydraulic press. Samples were made on a hydraulic press of the “HJ0802” brand at a force of 7 tons with the following dimensions: diameter (d) = 20 mm, height (h) = 20–25 mm. The ratio of components (Al – SiO₂) of the mixtures was calculated by stoichiometry. SHS compositions were placed in a furnace heated to 950 °C, after technological combustion they were kept for 30 min to cool the samples.

The combustion temperature was measured by pyrometric thermometers of the DT-8869H brand. The temperature of the sample was measured throughout the combustion process. After SHS, the phase composition of the synthesized materials was determined, the density, strength and thermal conductivity of the samples were measured.

Scanning electron microscopy was performed on a Quanta 3D 200i Dual system device and allows obtaining images of the powder surface. Elemental analysis of the obtained composites was performed by recording a spectrometer, which is capable of determining the spectral lines of characteristic radiation from atoms of chemical elements. Spectral lines corresponding to the elements contained in the sample are automatically identified, and the intensities of these lines are determined. In this case, the line intensity is proportional to the concentration of the element in the composition.

Research results and their discussion

The results of the electron microscopy study of ash and fly ash showed that the original contains a large number of meso- and micropores, which reduce thermal conductivity; such materials have high heat resistance and chemical stability.

SEM images show that in the initial state the size of ash particles is up to 30 μm and has a spherical, porous structure. After MCT the surface of the particles was destroyed and the size of the particles decreased. Figure 3b shows that the surface of the particles after MCT is more lamellar.

The particles of the initial fly ash are spherical in shape and have a porous structure. After MCT, it is evident that the correct spherical shape of the particles is destroyed and the particle size decreases.

A study was conducted of the structure and dispersion of particles of technogenic waste (ash and fly ash) depending on the conditions of mechanochemical treatment. An assessment was made of the bulk density of ash and fly ash after various MCT modes (Table 1).

The bulk density of ash decreases, and fly ash increases with increasing time of MCT. The results obtained indicate that MCT provides a significant change in the structure, and, consequently, the activity of the powders under study.

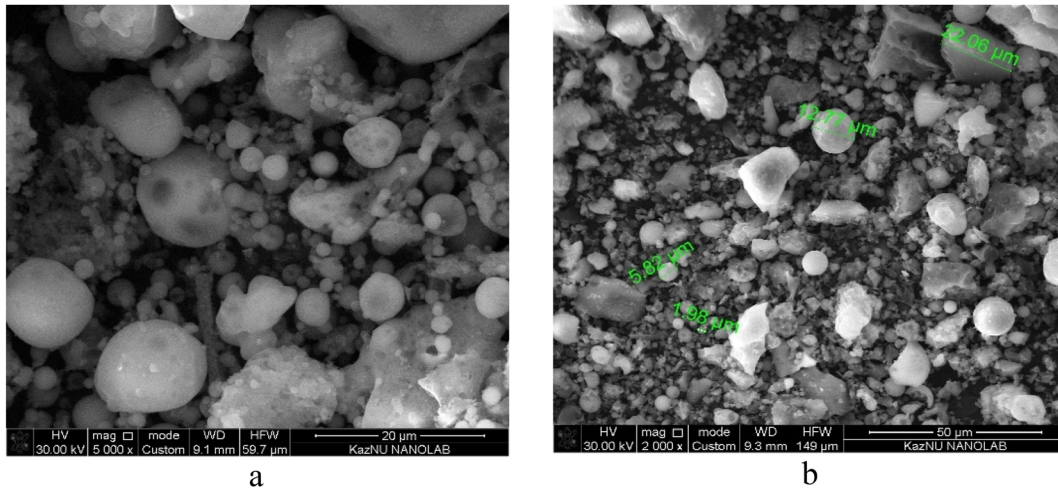


Fig. 3: SEM images: (a) initial ash; (b) ash after MCT ¼ 20 min.

Table 1: Bulk density of ash and fly ash powder depending on the conditions of the MCT.

Material, M_p/M_b	Bulk density, g/cm ³		
	MCT time, min		
	10	20	30
Ash, 1/2	1	0.95	0.91
Ash, 1/4	1.2	1.15	1.09
Fly ash, 1/2	0.87	0.91	0.96
Fly ash, 1/4	0.74	0.82	0.83

To ensure dispersion and modification of the surface of technogenic waste particles, modifiers were introduced into the ground powder as in the case of diatomite.¹¹ Similar systematic studies of the structure were carried out, as for diatomite, and optimal conditions for MCT were determined during the synthesis of composite particles modified with graphite, polyvinyl alcohol and stearic acid. To assess the substructural features of technogenic waste particles, they were studied using the SEM method (Fig. 4).

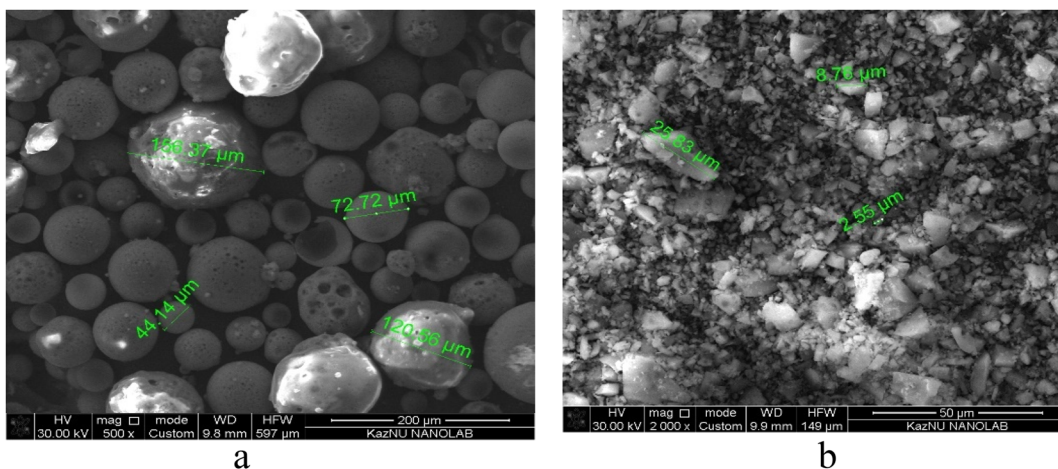


Fig. 4: SEM images: (a) initial fly ash (AF); (b) fly ash after MCT 20 min 1/4.

From the presented figures it can be seen that during MCT of technogenic powder in the presence of a modifier the destruction of particles increases, the number of small particles encapsulated in a structured shell increases (Fig. 5). Under the influence of an electron beam the particles of the sample are often transformed and acquire the shape of spheroids, which indicates the high activity of the modified particles. The noted fact of the increase in the activity of ash and slag particles after MCT with a graphite modifier and the change in their structure under mechanical action. Also, when activating and modifying ash and fly ash with polyvinyl alcohol, the effect of destruction of spherical particles increases, since alcohol in the modifier is an activator of destruction. Carbon, in the form of small crystals, enters the film on the surface of dense monocrystalline particles and forms an independent loose formation of rounded particles. After MCT with stearic acid, sample particles of about 2–3 μm in size are encapsulated in a sufficiently dense formation. Fragments in the form of flattened rounded particles are observed at the boundaries of the particles. Thus, there is a specific effect of the modifier on the structure of silicate compounds.

During MCT, in addition to external morphological changes in ash and fly ash particles, accumulation and transformation of the defect structure occurs, which is reflected in the change in the crystallite size. The crystallite size and X-ray line broadening were measured in three planes with the determination of the average value (Table 2).

The study of the patterns of structural changes in ash and fly ash particles during MCT was carried out for 20 min of treatment as the optimal time, according to the results of powder density studies. An increase in the number of grinding balls (i.e., M_b in the ratio M_p/M_b), and therefore an increase in the number of blows and deformation intensity, leads to a decrease in the crystallite size. If for ash ground without modifiers, the crystallite size at $M_n/M_{sh} = 1/2$ was 720 $\text{\AA}$, then after processing in the presence of a modifier, the crystallite size increased significantly. A similar pattern is observed for fly ash. Probably, the presence of modifiers during MCT of ash and

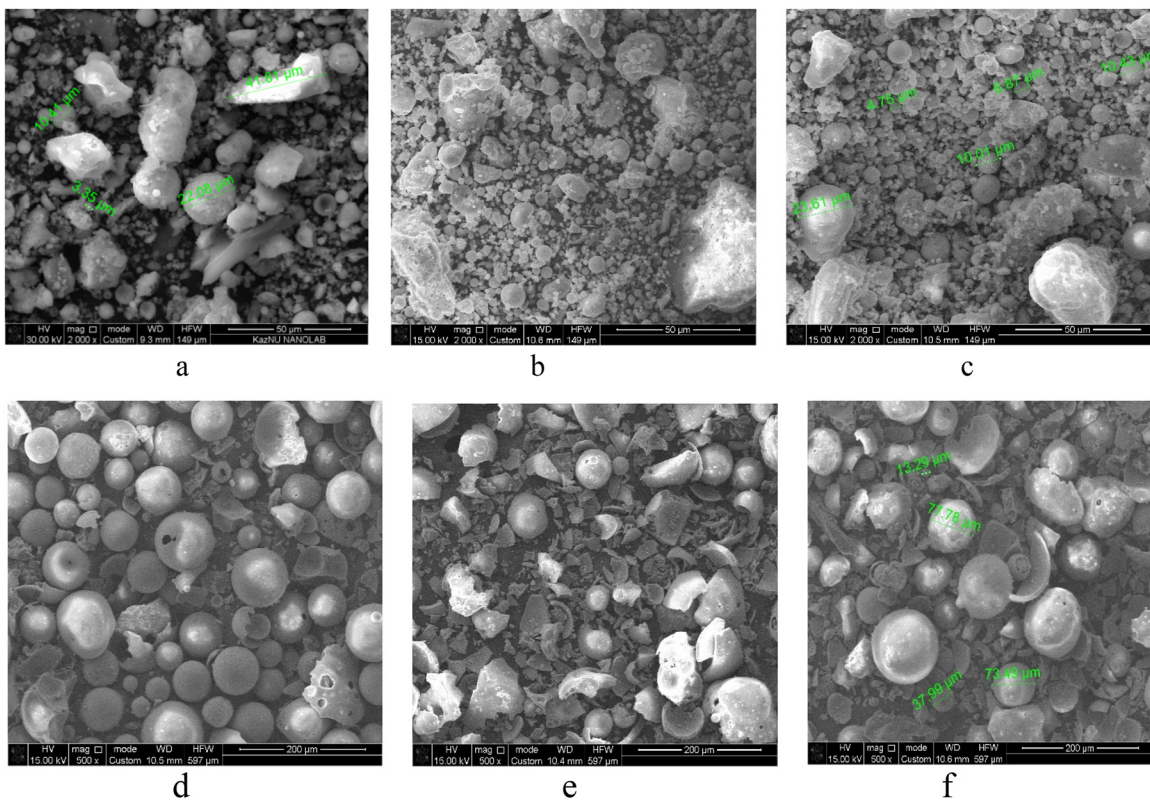


Fig. 5: SEM images of ash and fly ash with graphite, polyvinyl alcohol and stearic acid, after 20 min MCT. (a) Ash + 10 % C, (b) ash + 10 % PVA, (c) ash + 10 % SA, (d) fly ash + 10 % C, (e) fly ash + 10 % PVA, (f) fly ash + 10 % SA.

Table 2: Change in the crystallite size of ash and fly ash particles as a result of MCT with a change in the M_p/M_b ratio and the type of modifier.

Modifier	Crystallite size, L, Å		
	Ratio of M_p/M_b		
	1/2	1/3	1/4
Ash	720	610	370
Ash + 10 % C	1060	650	410
Ash + 10 % PVA	1490	700	440
Ash + 10 % SA	1360	620	470
Fly ash	680	540	430
Fly ash + 10 % C	990	680	470
Fly ash + 10 % PVA	1670	1120	580
Fly ash + 10 % SA	1560	1080	490

fly ash promotes the annihilation of defects as a result of their diffusion to the particle surface and the formation of compounds and structural compositions with the participation of elements of the destroyed modifier.

Self-propagating high-temperature synthesis (SHS) is an energy-saving technology, with the help of which in this work heat-insulating materials were obtained based on pre-mechanically activated technogenic waste. The results of the conducted studies indicate a significant influence of preliminary mechanochemical treatment on the development of combustion processes in the self-propagating high-temperature synthesis system. It was found that the activation of the batch components and their subsequent modification with various compounds leads to a change in the combustion parameters, in particular the induction period and maximum temperature.^{12,13}

Table 3 shows the results of determining the compressive strength and thermal conductivity of the samples after SHS for technogenic waste. The results showed that thermal insulation materials based on the original ash and fly ash have a maximum temperature of 1100 °C, a thermal conductivity coefficient of 0.175 W/m K, strength of 7.63 MPa and moisture adsorption of 0.32 kg/(m² min). Samples based on ash and slag after MCT have the lowest thermal conductivity coefficient of 0.098 W/m K, the highest strength index of 35.53 MPa and a moisture adsorption degree of 0.28 kg/(m² min). Mechanical treatment has a noticeable positive effect on the original ash and fly ash, improving its structure and heat resistance. Thus, it is a good heat insulator with the best characteristics. Heat insulators based on ash + 10 % C showed the following characteristics: $T_{\max}$: 1215 °C – the highest among all heat insulating materials based on ash, thermal conductivity coefficient of 0.114 W/m K,

Table 3: Strength and SHS coefficient values of ash-based materials, modifier content was 10 %.

Samples	$T_{\max}$, °C	Strength, MPa	Thermal conductivity coefficient, W/(m K)	Initial adsorption rate, kg/(m ² min)
Ash initial	1100	7.63	0.175 ± 0.02	0.32
Ash 1/4 20 мин МСТ	1133	35.53	0.098 ± 0.02	0.28
ЗШ + графит ¼ 20 min МХО	1215	19.86	0.114 ± 0.02	0.79
Ash + PVA ¼ 20 min МСТ	1213	0.00	0.197 ± 0.02	1.50
Ash + SA ¼ 20 min МСТ	1161	29.26	0.149 ± 0.02	0.37
Fly ash initial	1117	8.36	0.160 ± 0.02	0.67
Fly ash 1/4 20 min МСТ	1136	16.72	0.097 ± 0.02	0.36
Fly ash + C ¼ 20 min МСТ	1125	9.20	0.163 ± 0.02	1.05
Fly ash + PVA ¼ 20 min МСТ	1248	0	0.238 ± 0.02	1.42
Fly ash + SA ¼ 20 min МСТ	1144	12.54	0.156 ± 0.02	0.75

strength – 19.86 MPa, and adsorption degree – 0.79 kg/(m² min). Thermograms show a clear shift of degradation and sintering peaks to higher temperatures. Carbon promotes the formation of a stable porous structure and reduces thermal conductivity. The resulting thermal insulation materials are suitable for high-temperature conditions. Samples based on fly ash + PVA are porous and thus show the lowest strength. Probably, the excess of organic matter (10 % PVA) leads to the formation of an unstable structure and burnout during heating. Heat insulators based on ash + SA have a thermal conductivity coefficient of 0.149 W/m K, strength of 29.26 MPa, adsorption of 0.37 kg/(m² min) and are heat insulators with good mechanical and insulating characteristics. Stearic acid additives improve combustion stability.

SHS thermal insulators based on fly ash (without treatment) have a maximum temperature of 1117 °C, thermal conductivity coefficient of 0.160 W/(m K), low mechanical strength of 8.36 MPa. The initial adsorption rate of 0.67 kg/(m² min) shows high moisture absorption capacity, which may be undesirable when used in high humidity conditions. SHS samples with fly ash after mechanochemical treatment (MCT) have $T_{\max}$ – 1136 °C, porosity – 11.61 %, thermal conductivity coefficient – 0.097 W/(m K). A significant reduction in thermal conductivity leads to improved thermal insulation properties. The strength of these samples is 16.72 MPa. A significant increase in strength by 2 times, the material has become significantly more resistant to mechanical loads. The initial adsorption rate of heat-insulating materials based on fly ash after MCT is 0.36 kg/(m² min), the indicator is almost 2 times lower than that of the original – good moisture-resistant behavior. MCT of fly ash particles significantly improves all characteristics – the material becomes stronger, less thermally conductive and moisture-resistant. This makes it the best option without any additional additives.

Thermal insulation materials with particles (fly ash + 10 % C after MCT) have the following characteristics: $T_{\max}$ – 1125 °C, thermal conductivity coefficient 0.163 W/(m K), worse than even that of the original material – the addition of carbon increased the thermal conductivity. The porosity of the SHS samples is significantly higher – the structure has become looser 18.04 %, the strength is 9.20 MPa. The initial adsorption rate is a significant increase in moisture absorption – 1.05 kg/(m² min). The addition of 10 % C after MCT had a negative effect on strength, moisture resistance and thermal conductivity. Despite the increase in porosity, the insulating properties have worsened.

The highest maximum temperature is observed in fly ash + 10 % PVA (1248 °C) – possibly due to improved thermal stability due to additives. PVA additives sharply increase moisture absorption to 1.42, which negatively affects durability.

Samples of fly ash + 10 % SA showed a moderate thermal conductivity coefficient of 0.156 W/(m K) and compressive strength up to 12.54 MPa. The SA additive is optimal for creating durable, sufficiently insulating and moisture-resistant materials.

The XRD results showed the presence of gamma-aluminum oxide, as well as silicon oxide, aluminum, silicon and iron silicide. In the synthesized samples, unreacted aluminum remains, which indicates that aluminum does not react with silicon oxide at all. This fact is an advantage for the obtained metal-ceramic samples, since the presence of aluminum in the product increases the strength of the material (Fig. 6).

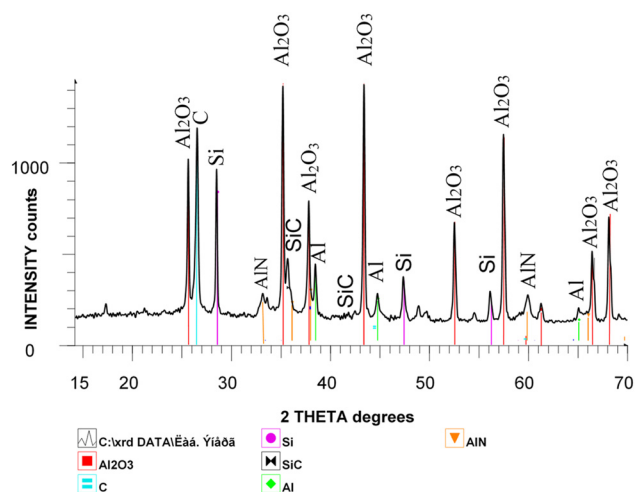


Fig. 6: Results of X-ray phase analysis of the SHS sample of ash + 10 % graphite after 20 min ratio $M_p/M_b = 1/4$ MCT.

The results of the study showed that the MCT of technogenic raw materials used as components of the charge mixture for the SH-synthesis of composite systems contributes to a change in the kinetic characteristics of the combustion process: a decrease in the induction period of ignition and an increase in the combustion rate, which is a consequence of the increased activity of the powders studied after the MCT.

The influence of the choice of modifier and preliminary treatment of particles on the thermal characteristics of heat-insulating materials based on fly ash and ash has been revealed, which can be useful for optimizing high-temperature synthesis processes and obtaining materials with specified properties. Heat insulators based on fly ash and ash, especially after mechanical and chemical treatment and the introduction of modifiers, are effective, heat-resistant and environmentally friendly materials that are superior to many traditional analogues. Thus, heat-insulating materials based on fly ash and ash are becoming increasingly relevant in industry and construction due to their low cost, availability and the possibility of recycling man-made waste.

Acknowledgments: We express our gratitude to the Ministry of Science and Higher Education of the Republic of Kazakhstan for funding the project.

Research ethics: Research ethics are observed.

Informed consent: Informed consent was obtained from all individuals included in this study, or their legal guardians or wards.

Author contributions: Sadykov B.S. – conceptualization, data curation, visualization, writing – original draft, writing – review & editing. Khairullina A.S. – formal analysis, investigation, methodology. Artykbayeva A.B. – investigation, methodology, resources. Maten A.E. – formal analysis, investigation, methodology. Zhapekova A.O. – conceptualization, formal analysis, methodology. Turesheva A. Zh. – formal analysis, investigation, methodology. Bakkara A.E. – conceptualization, data curation, supervision, writing – original draft, writing – review & editing.

Use of Large Language Models, AI and Machine Learning Tools: None declared.

Conflict of interest: The author states no conflict of interest.

Research funding: This work was supported by the Ministry of Science and Higher Education of the Republic of Kazakhstan (grant number: AP19680089).

Data availability: Not applicable.

References

1. Liu, M.; Zhu, P.; Yan, X.; Li, H.; Chen, X. The Application of Solid Waste in Thermal Insulation Materials: A Review. *J. Renew. Mater.* **2024**, *12* (2), 329–347. ISSN 2164-6325. <https://doi.org/10.32604/jrm.2023.045381>.
2. Zhu, L.; Li, S.; Li, Y.; Xu, N. Novel Applications of Waste Ceramics on the Fabrication of Foamed Materials for Exterior Building Walls Insulation. *Constr. Build. Mater.* **2018**, *180*, 291–297. ISSN 0950-0618. <https://doi.org/10.1016/j.conbuildmat.2018.05.290>.
3. Liu, Y.; Kumar, D.; Lim, K. H.; Lai, Y. L.; Hu, Z.; Ambikakumari Sanalkumar, K. U.; Yang, E.-H. Efficient Utilization of Municipal Solid Waste Incinerator Bottom Ash for Autoclaved Aerated Concrete Formulation. *J. Build. Eng.* **2023**, *71*, 106463. ISSN 2352-7102. <https://doi.org/10.1016/j.jobe.2023.106463>.
4. Torkittikul, P.; Nochaiya, T.; Wongkeo, W.; Chaipanich, A. Utilization of Coal Bottom Ash to Improve Thermal Insulation of Construction Material. *J. Mater. Cycles Waste Manag.* **2015**, *19* (1), 305–317; <https://doi.org/10.1007/s10163-015-0419-2>.
5. Chen, G.; Yang, F.; Zhao, S.; Li, K.; Chen, J.; Fei, Z.; Yang, Z. Preparation of High-Strength Porous Mullite Ceramics and the Effect of Hollow Sphere Particle Size on Microstructure and Properties. *Ceram. Int.* **2022**, *48*, 19367–19374. <https://doi.org/10.1016/j.ceramint.2022.03.231>.
6. Basu, M.; Pande, M.; Bhadoria, P. B. S.; Mahapatra, S. C. Potential Fly-Ash Utilization in Agriculture: A Global Review. *Prog. Nat. Sci.* **2009**, *19*, 1173–1186; <https://doi.org/10.1016/j.pnsc.2008.12.006>.
7. Burgonutdinov, A.; Khusainova, K. Possible Technologies for Using Fly Ash. Transport. Transport Facilities. *Ecology* **2022** (1), 36–44; <https://doi.org/10.15593/24111678/2022.01.05>.
8. Shao, W.-C.; Lu, C.-L.; Dong, Y.-W.; Chen, J.-W.; Chiang, Y.-T. Research on Innovative Green Building Materials from Waste Oyster Shells into Foamed Heat-Insulating Bricks. *Clean. Mater.* **2024**, *11*, 100222. ISSN 2772-3976. <https://doi.org/10.1016/j.clema.2024.100222>.
9. Mofa, N. N.; Sadykov, B. S.; Bakkara, A. E.; Mansurov, Z. A. Fabrication of Metal Powders for Energy-Intensive Combustible Compositions Using Mechanochemical Treatment: 2. Structure and Reactivity of Mechanically Activated Al-Modifier–SiO₂ Mixtures. *Russ. J. Non-Ferr. Met.* **2019**, *60*, 694–703. <https://doi.org/10.3103/S1067821219060130>.

10. Mansurov, Z. A.; Mofa, N. N.; Sadykov, B. S.; Sabaev, Zh. SHS Production of Heat-Shield Materials from Minerals and Residual Products: Influence of Preliminary Mechanochemical Treatment and Modifying Agents. *Int. J. Self-Propag. High-Temp. Synthesis* **2016**, 25 (3), 166–172; <https://doi.org/10.3103/S1061386216030080>.
11. Sadykov, B.; Khairullina, A.; Artykbayeva, A.; Maten, A.; Zhapekova, A.; Osserov, T.; Bakkara, A. High-Temperature SHS Heat Insulators Based on Pre-activated Mineral Raw Materials. *Crystals* **2024**, 14, 904. <https://doi.org/10.3390/cryst14100904>.
12. Mansurov, Z. A.; Mofa, N. N.; Sadykov, B. S.; Antonyuk, V. I. Mechanochemical Treatment, Features of the Structure and Properties, and Reactivity of SHS Systems Based on Natural Materials 3. Influence of Mechanochemical Treatment and Modification of Oxide Materials on the Technological Combustion. *J. Eng. Phys. Thermophy.* **2014**, 87, 1094–1102. <https://doi.org/10.1007/s10891-014-1111-4>.
13. Mansurov, Z. A.; Mofa, N. N.; Sadykov, B. S.; Sabaev, Zh. SHS Production of Heat-Shield Materials from Minerals and Residual Products: Influence of Preliminary Mechanochemical Treatment and Modifying Agents. *Int. J. SHS* **2016**, 25 (3), 166–172; <https://doi.org/10.3103/S1061386216030080>.
14. Thermal Conductivity Coefficient of Brick in Comparison with Other Materials [Koeffitsient teploprovodnosti kirpicha v sravnenii s drugimi materialami]. <https://jsnip.ru/normy/kirpichteplprovodnost>.