

CHARACTERIZATION AND POSSIBILITIES FOR UTILIZATION OF INDUSTRIAL WASTES FROM PROCESSING, BENEFICIATION OF MINERALS, AND SMELTING

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Received 12 November 2025

Accepted 29 April 2026

DOI: 10.59957/jctm.v61.i4.2026.12

ABSTRACT

The aim of this study is the characterization of some of main inorganic wastes for Bulgaria as slag and ash from lignite - fired power plants, clinker and lead slag from the lead and zinc smelting industry, and fayalite waste from copper smelting production. The chemical and phase compositions and particle size distribution of the waste materials were determined using XRF, XRD and laser diffraction, respectively. Hot stage microscope was used to evaluate the thermal behaviour of the samples. SEM was used to study the microstructure of the sample.

The studied wastes contain mainly oxides of silica, aluminium, calcium and iron which also are basic for the building ceramics. In addition, they are finely dispersed with particle sizes below 1 mm, so they can be used without crushing or milling. However, due to the various and complex mineralogical composition the samples are characterized with different thermal behaviour.

The fly ash contains high percentage of amorphous phase, together with plagioclase, magnesium ferrite, quartz and some gypsum. As a result, it is chartered with wide firing interval at about 1200°C and can be considered as a main raw material for new building ceramics.

The lead slag contains less aluminium and silica and main crystal phases from the melilite group. It easy forms liquid phase at lower temperatures, so that can be considered as an alternative flux.

Finally, the waste from copper smelting production, which mainly contain fayalite and magnetite, melts at the highest temperature. It cannot be considered as a flux but can be used as a filler in ceramic batches or as raw material for geopolymers as well.

From the studied wastes only the bottom ash, due to the extremely high gypsum content, and the clinker slag, because of presence of high amount carbon and metal iron, are not appropriate for direct usage in ceramic industry.

Keywords: industrial wastes, fly ash, bottom ash, fayalite, clinker slag, blast - furnace slag, ceramics, thermal behaviour.

INTRODUCTION

Industrial waste production has grown significantly worldwide over the past decades. This increase is driven by factors such as population growth, urbanization, economic development, and consumer shopping habits.

Fig. 1 shows the ten countries in Europe with the

highest total waste generation per capita, including Serbia [1].

The highest amounts were recorded in Finland, where an average of 20 tons of waste per person was produced in 2022. This is followed by Estonia with 16.8 t, Sweden with 15.6 t, Luxembourg with 15.2 t, and Bulgaria with 14.6 t per capita. Bulgaria's figure is

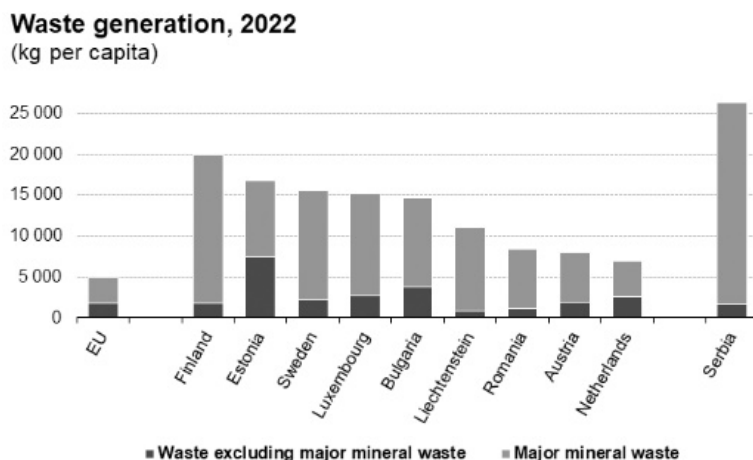


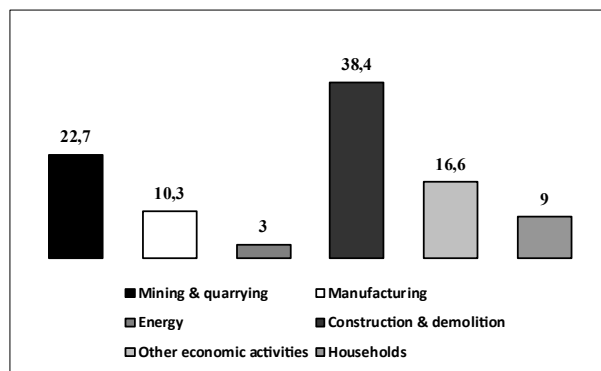
Fig. 1. Ten European countries with the highest total waste generation in 2022 (kg per capita).

about three times higher than the EU average of 5 t per person. The elevated waste levels in Finland and Sweden are mainly due to a booming metal mining industry in both countries, whereas in Bulgaria, the high waste production is primarily linked to coal mining, mineral extraction and processing, smelting, and coal power plants [2].

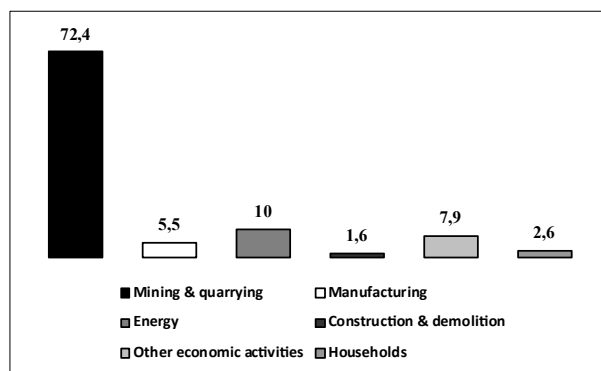
Fig. 2 shows the distribution of waste generated by economic activities and households in the EU and Bulgaria. Construction and demolition (C&D) waste accounts for 38.4 % of total waste in the European Union, whereas in Bulgaria it represents only 1.6 %. In contrast, mining and quarrying (M&Q) waste accounts for as much as 72.4 % of total waste in Bulgaria, compared to 22.7 % in the EU. This difference can be explained by the significant share of the mining industry in the Bulgarian economy. Therefore, a detailed study of the types of available waste and the potential method for their utilization is of great importance [3]. These M&Q wastes are mainly inorganic and consist largely of silica, alumina, lime or iron rich residuals which could be used in production of various construction materials.

Coal gangue generated by mining activities represents the largest proportion of these waste streams in Bulgaria [4, 5]. Its utilization potential has already been studied, and the results were reported in our previous study [6]. That preliminary assessment indicated that clays are suitable as raw materials for the ceramic industry and for geopolymer production. Accordingly, the present report focuses on the other

major M&Q wastes streams in Bulgaria and discusses possible recommendations and examples for their use as raw materials in high-volume construction applications.



a)



b)

Fig. 2. The distribution of waste generated by economic activities and households in EU (a) and Bulgaria (b) respectively in 2022 (% share of total waste).

EXPERIMENTAL

This study investigates several types of waste generated in Bulgaria because of mining, mineral processing and beneficiation, and metallurgical operations. The analysed materials included bottom and fly ash from the lignite-fired thermal power plants “Maritsa East 2” and “AES ContourGlobal” (designated C_1 and C_2 , respectively); fayalite derived from copper slag produced at the “Aurubis-Pirdop” smelter (C_3); clinker, lead slag, and zinc slag from the “KCM-Plovdiv” smelter (C_4 and C_5 , respectively); and blast furnace slag from “Kremikovtzi” (C_6).

The chemical composition of the collected samples was determined by X-ray fluorescence (XRF) using a Zetium Spectrometer (Malvern Panalytical). Particle size distribution was measured by laser diffraction with a Mastersizer 3000 instrument (Malvern, UK). Mineralogical and phase composition was further assessed by powder X-ray diffraction (XRD) using an automatic Philips diffractometer system equipped with a PW1830 generator and a PW1050 goniometer.

Hot Stage microscope (HSM) (MISURA 1400) was applied for evaluation of the thermal behaviour of the wastes. Small samples, suitable for direct measurements, with standard cylindrical shape of 5 mm height and 2 mm diameter were prepared by manually pressing with a plunger and distilled water used as a binder.

RESULTS AND DISCUSSIONS

Ferrous metallurgy in Bulgaria was operating in Kremikovtzi industrial area from 1963 until 2008. The wastes from iron extraction for this period had been stored in slag dumps. There is no specific information available about quantity of blast - furnace slag from the steel mill.

It is well known from the practice that blast - furnace slag is used as a raw material in the cement industry [7 - 9]. It is also suitable for production of various glass - ceramics [3, 10]. The first product named “Slagsitalls” has been produced since 1966, only a decade after the discovery of glass ceramics by D. Stookey [11].

Several Bulgarian scientific teams have also worked with this waste, and it has been well characterized [3, 12 - 16].

The bottom ash and fly ashes were collected at Thermal power plant “TPP Maritsa Iztok - 2” and “AES

ContourGlobal” respectively. These are Bulgaria’s largest thermal power plants that relies on the lignite coal from the “Maritsa Iztok mines”. The operations generate substantial fly ash (estimated at 0.2 - 1.2 million t/year), bottom ash (approximately 0.12 - 0.6 million t/year), gypsum from FGD (around 0.2 - 0.5 million t/year, depending on sulfur content and operational units). The wastes are store in ash ponds, heaps or landfills.

“Aurubis - Pirdop” plant is the largest copper smelter and refinery in southeastern Europe, producing copper anodes, cathodes and sulfuric acid. The main byproduct is fayalite (Fe_2SiO_4) generated foam of the copper smelting process, specifically during the smelting of copper concentrates and converter slag processing. The annual fayalite production is in the range of 0.3 - 0.63 million tons depending on operational efficiency, slag composition, and flotation recovery rates. “Aurubis - Pirdop” stores fayalite in a fayalite tailings pond.

“KCM - Plovdiv” is the largest lead and zinc smelter in Bulgaria and a leading producer of non - ferrous and precious metals in Southeastern Europe. The plant generates slags as byproducts of its pyrometallurgical processes - approximately 70 000 - 150 000 t per year. The slags are store in waste heaps.

X-ray fluorescence (XRF) analyses

The results of chemical XRF analysis of main elements of the industrial wastes are presented in Table 1.

It is shown that the wastes contain the main chemical elements that are used for the ceramic industry - Si Al Ca and Fe. The silicon varies in the samples from 21.0 % in C_2 to 4.8 % in C_4 . The aluminium is highest in the fly ash - 11.4 % and lowest in the clinker slag - 4.8 %. The highest content of calcium is in C_4 - 31.9 % and in C_6 - 28.9 %. The content of iron is highest in fayalite - 64.3 % and lowest in blast - furnace slag - 0.7 %.

Additionally, from samples 2 to 5 about 0.2 - 2.9 % sulphur is measured (excluding sample 1 where the content is about 11.9 %). The reason is the adding in the bottom ash wastes from the desulfurization in power plant.

The magnesium content from samples 1 to 6 is relatively low from 0.6 % to 3.1 % while the alkali varies from 0.2 % to 1.4 %.

The chemical XRF analysis shows that only the bottom ash is not suitable for use in ceramic industry because of high sulphur content.

Table 1. Results from chemical analysis of main elements of the studied samples (wt. %).

Powders Elements	Bottom ash C ₁	Fly ash C ₂	Fayalite C ₃	Clinker slag C ₄ Fe dusts	lead and zinc slag C ₅	Blast - furnace slag C ₆
Si	14	21.0	14.6	4.8	9.3	16.4
Al	7.1	11.4	2.5	2.2	3.7	4.9
Ca	20.4	13.3	2.3	31.9	27.3	28.9
Fe	30.7	28.7	64.3	40.9	28.6	0.7
O	11.5	16.4	8.3	9	13.6	-
S	11.9	2.9	0.2	2.2	1.8	-
Mg	1.1	1.6	0.6	1.0	1.1	3.1
Ti	0.9	1.0	0.3	0.3	0.4	-
K	1.0	1.4	1.4	0.2	0.6	0.8
Na	0.3	1.2	0.6	0.3	0.9	0.2
Zn	-	-	2.8	0.5	4.7	-
Cu	-	-	0.6	0.7	0.7	-
Pb	-	-	0.5	0.6	2.5	-
Mn	0.2	0.2	0.1	4.1	2.1	2.0
Ba	0.3	0.3	0.1	0.3	0.4	2.9
Other	0.6	0.6	0.8	1.0	2.3	40.1

Laser diffraction

In general, the investigated industrial wastes are characterized by a fine-grained particle size, which is favourable for their practical utilization. Representative particle size distribution data for samples C₁ and C₂ are presented in Figure 3. The median particle size (d50) was determined to be approximately 77.9 μm for the fly ash and 171 μm for the bottom ash, confirming the finer nature of the fly ash fraction.

Fayalite waste has 90 % finer - grained size of 87.8 μm. These increase possibilities for its application. The typical result from particle size of C₃ is shown in Fig. 4.

The typical results from particle size of C₄ and C₅ are presented in Fig. 5 and show that the other studied wastes - clinker slag Fe dust and Pb slags are also finer - grained (about 90 % of the particle size is below 99.4 μm).

The results show that all studied samples are finer - grained and can be used without prior crushing or milling.

X-Ray diffraction (XRD) analyses

The XRD results of C₁ (Fig. 6) show typical for similar wastes phases as gypsum (G main) - CaSO₄·2H₂O,

graphite 3R (Gr) - C, albite low (A) - NaAlSi₃O₈, magnetite (M) - Fe₃O₄ and quartz low (Q) - SiO₂. As it is already noted above the high gypsum amount is a result of mixing of bottom ash with desulfurization products.

In the XRD pattern of C₂ (Fig. 6) are presented phases as albite (A), magnesium ferrite (Mf) - MgFe₂O₄, gypsum (G) and quartz low (Q) as well as intensive

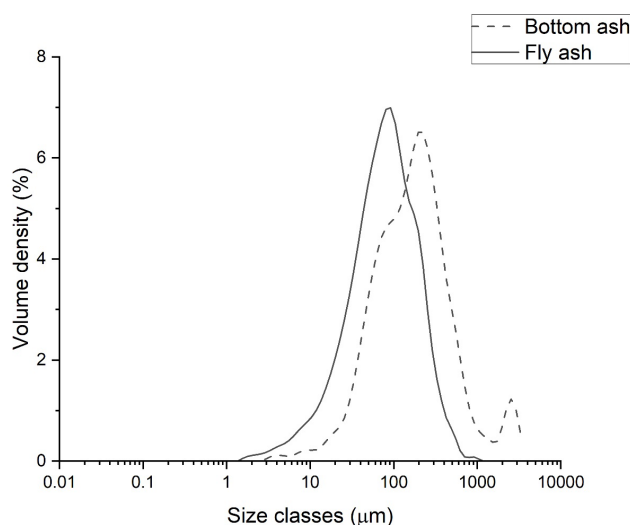


Fig. 3. Results overlay of bottom and fly ash.

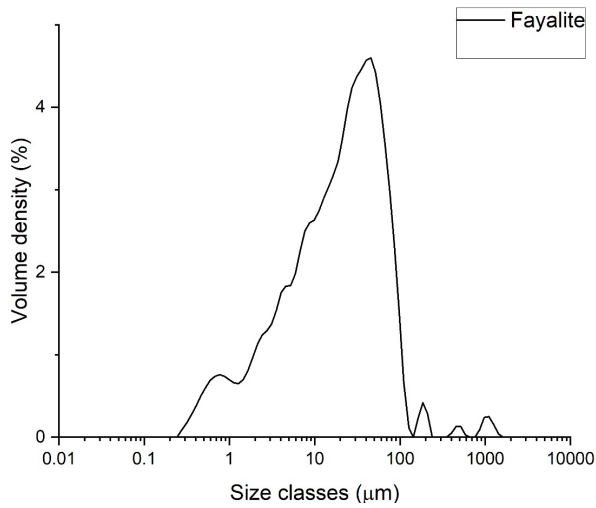


Fig. 4. Results overlay of fayalite.

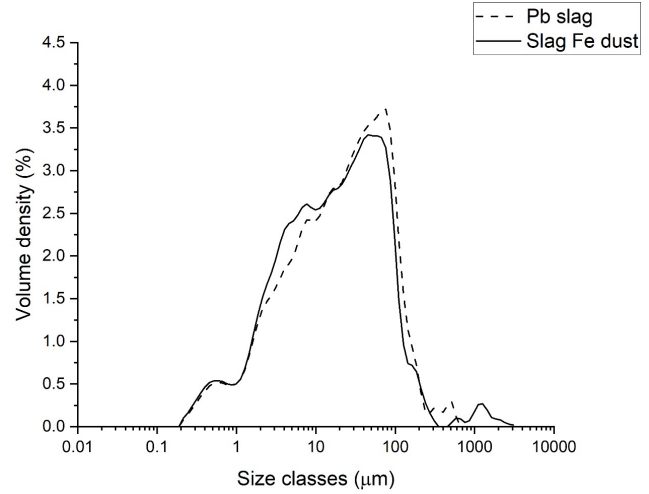


Fig.5. Results overlay of clinker slag Fe dust and Pb slag samples.

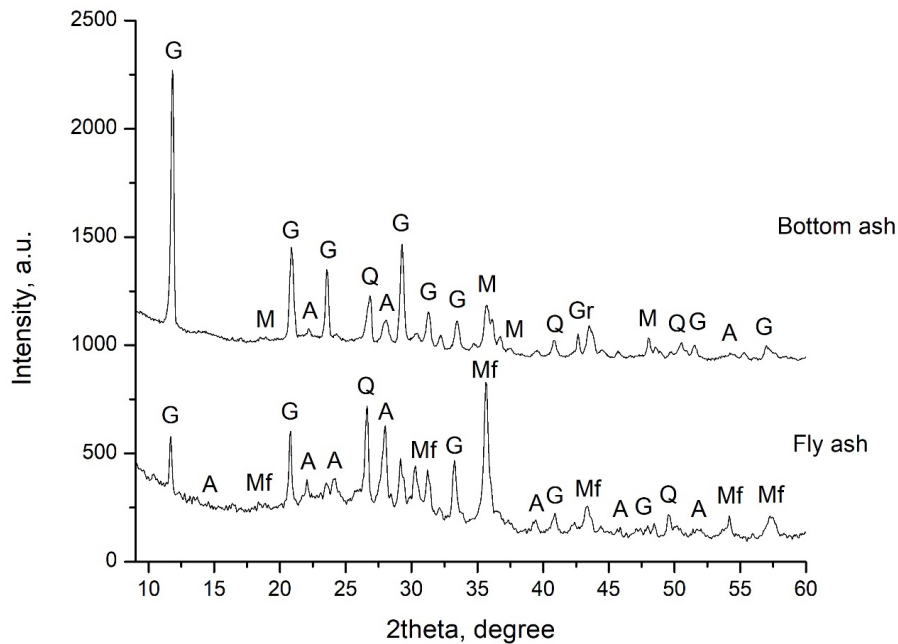


Fig. 6. Phase analysis of bottom ash (C_1) and fly ash (C_2) samples.

amorphous halo. The phase composition is like one of the bottom ashes excluding high amount of gypsum. The high amount of glassy phase presented in the bottom ash can improve the processes of sintering and geopolymerization. This means that only the fly ash, due to the lower % of sulphur, can be considered as alternative raw material.

The XRD results of C_3 (Fig. 7) shows higher crystallinity than of C_1 and C_2 and main crystal phases as magnetite (M) and fayalite (F) - Fe_2SiO_4 .

The XRD results of C_5 (Fig. 7) where the iron oxides percent is lower shows phases as akermanite - gehlenite (A - G) - $Ca_2Mg(Si_2O_7)$ and quartz low (Q). The figure shows that there is no metal iron in this sample.

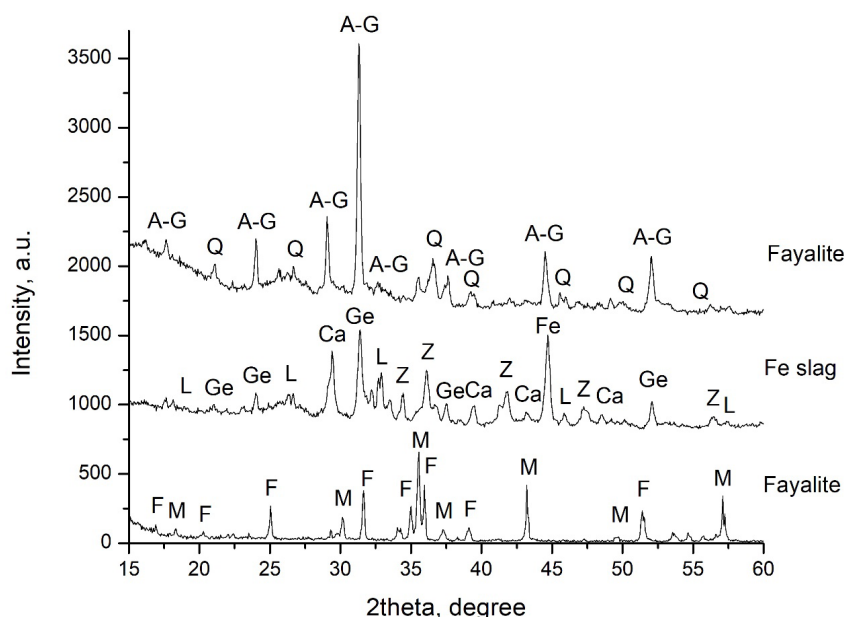


Fig. 7. Phase analysis of fayalite (C_3), clinker slag Fe dust (C_4) and Pb slag (C_5) samples.

Scanning electron microscopy (SEM) analyses

SEM of the studied wastes is presented in Fig. 8a, 8b, 8c, 8d and 8e. In general, all SEM results confirm the size distribution of the samples' particles.

The comparison of the waste in Fig. 8a and Fig. 8b shows that the fly ash is composed mainly of micrometer-size vitreous silica-based spheres that are smaller in size than these of the bottom ash. This result confirmed the size distribution of the material from Fig. 3. The bigger crystals in C_1 are mainly gypsum and in C_2 the spheres amounting to 60 - 80 %. The observed spherical shape is typical for a semi amorphous structure [3].

The SEM of fayalite sample (Fig. 8c) confirmed the results presented on Fig. 4. They are related to the presence of a small and large phase, the first one probably being a fayalite and the second one is a magnetite. The habit of these particles confirmed high crystallinity of sample.

Finally, Fig. 8d and Fig. 8e confirmed the complex composition of slags C_4 and C_5 .

Hot stage microscope (HSM) analyses

In the last part of the analysis, HSM results are given, which provides additional information about the possibilities for using the studied waste in the ceramic

industry.

The sintering plot and HSM silhouettes of C_1 and C_2 are reported on Fig. 9. Despite of the higher gypsum content in C_1 they have a similar behaviour and demonstrates starting of sintering at 1186°C for bottom ash and at 1214°C for fly ash. It is visible from the Fig. 9 that the softening of both samples begins at 1290°C, the melting of the bottom ash at 1305°C and of the fly ash at 1316°C. The sintering interval between temperature of sintering and temperature of softening of fly ash is about 100°C which means that it can be considered as a basic raw material in the ceramic production. A similar fly ash may be also used as a filler in the cement, concrete and bricks [12, 17, 18], geopolymers, in construction industry [3].

Hot Stage Microscope was applied for evaluation of the thermal behaviour of the fayalite (C_3) and clinker slag (C_4) for the purpose of the study. The sintering plot and HSM silhouettes are reported on Fig. 10 and demonstrate starting of sintering at 1174°C for clinker slag. The softening begins at 1206°C for C_4 and at 1315°C for C_3 . It is visible from the figure that both wastes have quite different thermal behaviour (the melting of clinker slag proceeds at 1213°C while fayalite melting takes place

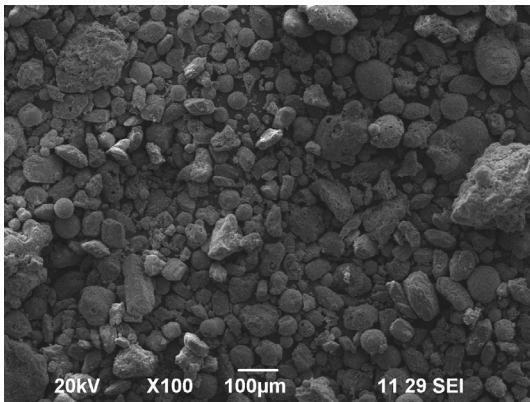


Fig. 8a. SEM of bottom ash.

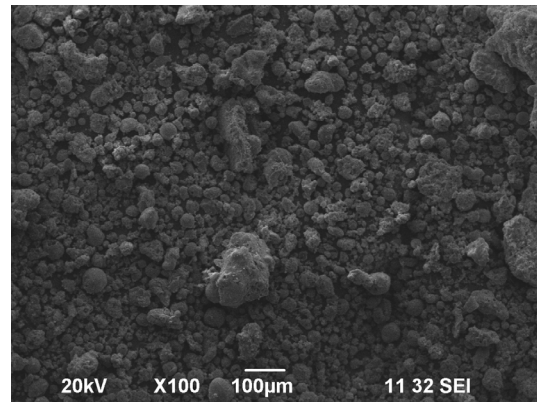


Fig. 8b. SEM of fly ash.

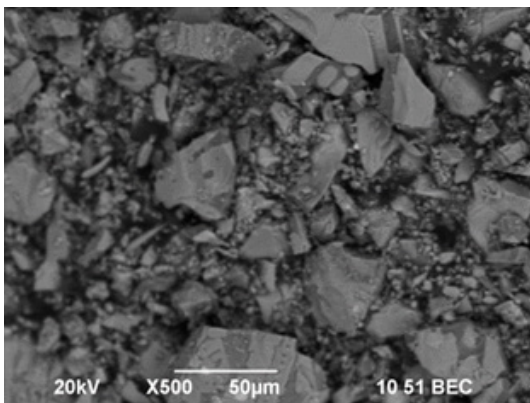


Fig. 8c. SEM of fayalite.

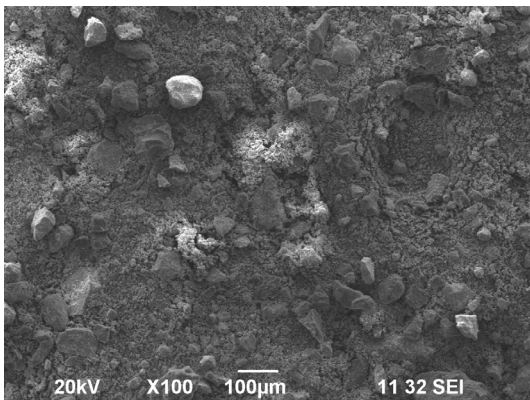


Fig. 8d. SEM of clinker 1 slag.

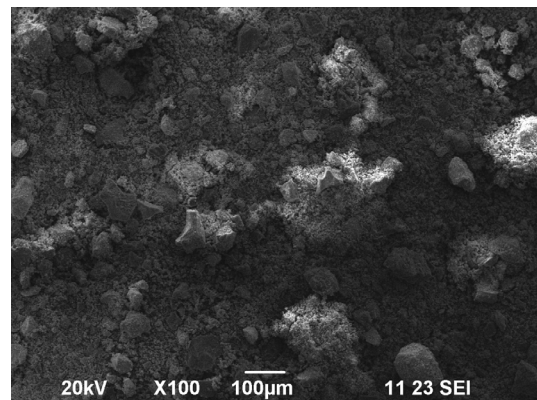


Fig. 8e. SEM of clinker 2 slag.

at a higher temperature).

The comparison of Fig. 9 and Fig. 10 shows that clinker slag has a somewhat similar thermal behaviour to fly ash but for C_4 the difference between temperature of sintering and temperature of softening is only 30 -

40°C. This lower sintering interval is only 30 - 40°C and acquires at lower temperature. Therefore, C_5 can be considered as a potential flux for ceramic production and can be mixed with suitable clays and other traditional raw materials [19]. Similar slags might find application

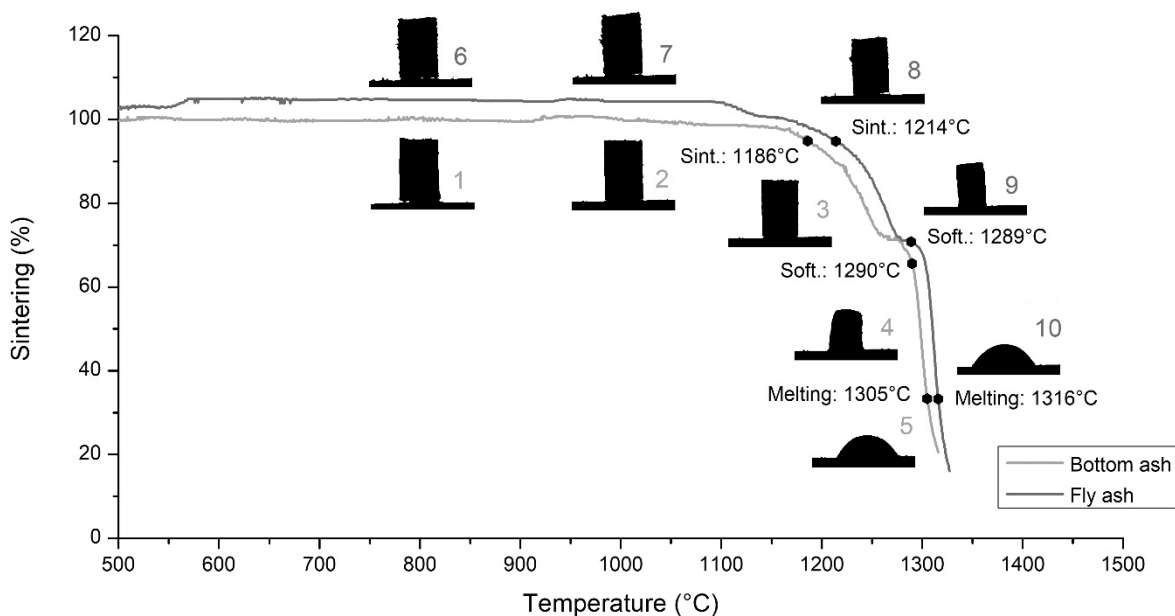


Fig. 9. Dilatometric sintering curve of bottom and fly ash.

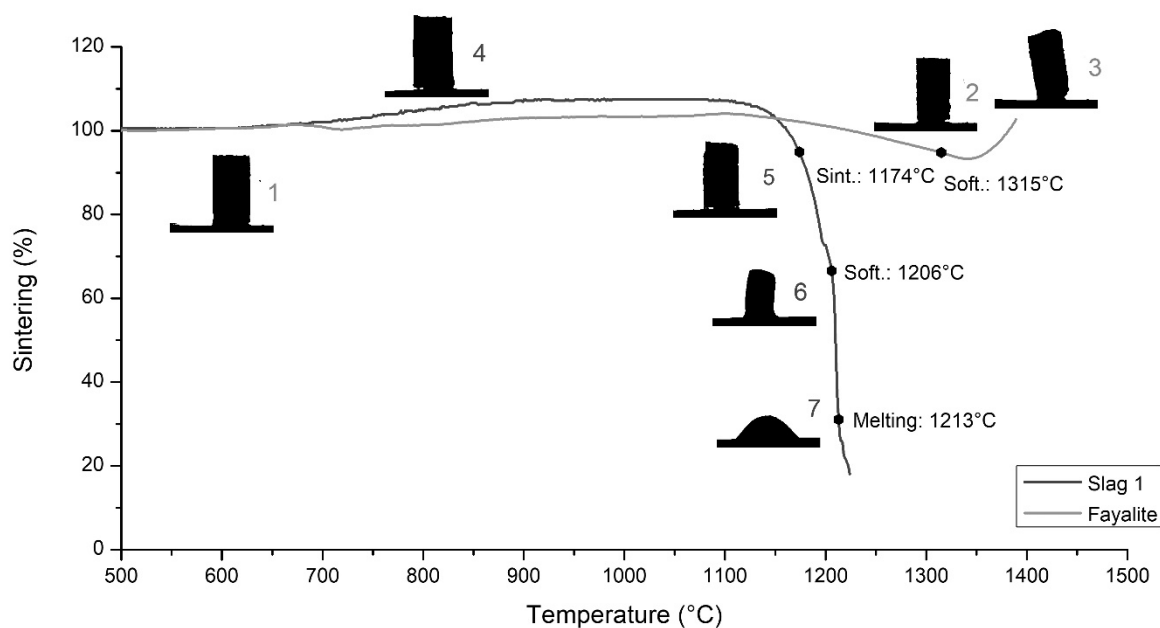


Fig. 10. Dilatometric sintering curve of clinker and fayalite slags.

as a raw material for the building and ceramic industries, production of concrete and geopolymers [19 - 21].

Unlike lead slag, fayalite does not form a large amount of liquid phase at low temperature [22]. This means that it can be used mainly like a filler. After

1200°C a trend of bloating is observed that provides a potential opportunity for obtaining foam materials [23]. Moreover, the fayalite slag (C_3) is appropriated for the synthesis of new iron - rich ceramics [3, 24] and geopolymers [23, 25, 26].

CONCLUSIONS

The results of the chemical, mineralogical, fractional and thermal analysis of studied wastes show that the main part of them are suitable for reusing in ceramic industry.

All studied wastes contain silica, aluminium, calcium and iron. In addition, they are finely dispersed having particle sizes below 1 mm. From the studied wastes only the bottom ash (C_1) due to the high gypsum content and the lead slag (C_4) due to the presence of metal iron are not appropriate as alternative ceramic raw material.

The fly ash (C_2) has a high content of SiO_2 and Al_2O_3 coupled with a high percentage of amorphous phase and a wide firing interval - about 1200 C. This means that it can be considered as a main raw material for new building ceramics.

Lead slag (C_3) contains less aluminium and silica but easily forms a liquid phase at lower temperatures. Therefore, it can be considered as an alternative flux.

Finally, fayalite (C_3) melts at the highest temperature so it cannot be considered as a flux. Similar residues can be used as a filler and a basic raw material for geopolymers as well.

Acknowledgements

This research was financially supported by The National Recovery and Resilience Plan (NRRP) project BG - RRP - 2.017 - 0024 - C01 "Using inorganic technogenic wastes in production of new construction materials with improved properties (WasteNewMat)". Some of the equipment used was acquired under Project BG16RFPR002-1.014-0015: "Clean technologies for sustainable environment-water, waste, energy for circular economy".

Authors' contributions

I.D., A.K.: conceptualization; I.D., A.K.: methodology; I.D.: validation; I.D., R.A., M.P., G.A.: formal analysis; R.A., M.P., G.A.: investigation; I.D.: writing-original draft preparation; A.K.: writing-review, editing and supervision. All authors have read and agreed to the published version of the manuscript.

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