Document: *"Final report of the bilateral research project between Austria and Nort Macedonia (Oead project number: MK2022)"*
Project funded by: *OeAD - Agentur für Bildung und Internationalisierung*
Project number: *MK2022*
Project uploaded to: *The report has been submitted on the OeaD (WTZ) online platform for project tracking*
Year of the report submission: *2024*

Finale report of the project *"Eco-based alkali-activated composites containing recycled aggregates''*

Introduction

The construction industry stands as a significant contributor to CO_2 emissions, with concrete production alone accounting for approximately 8-9% of global anthropogenic greenhouse gas emissions. This is largely attributed to the energy-intensive production of Portland cement clinker, the primary binder in concrete, which emits nearly 0.8-1.0 kg of CO_2 per kg of cement produced. The extraction of natural aggregates, comprising up to 70% of concrete volume, further increases environmental concerns, leading to resource depletion and ecological damage. In response to mounting environmental pressures, various European directives prioritize waste reduction and promote recycling and reuse initiatives within the construction sector. Efforts are underway globally to develop ecologically sustainable composites as alternatives to conventional concretes. Research endeavors are generally focused on two fronts: identifying low-CO_2 binders to replace Portland cement using industrial waste by-products, and substituting natural aggregates with recycled aggregate sourced from construction and demolition waste (CDW). A common approach to reducing Portland cement in concrete involves the partial or total replacement with supplementary cementitious materials (SCMs), such as fly ash from coal combustion in thermal power plants or granulated blast furnace slag from iron production. Alkali activation processes offer a pathway to develop binders primarily from waste materials, wherein alkali hydroxide and silicate solutions dissolve aluminosilicate-based materials, forming alkali-aluminosilicate gels and zeolitic phases. This process has demonstrated success, particularly with coal fly ash, a significant by-product of thermal power plants. In the Republic of North Macedonia, where coal predominates in electricity generation, fly ash utilization is primarily confined to the cement industry, with substantial quantities ending up in landfills. Innovative applications for fly ash are urgently needed. Similarly, the efficient reduction of natural aggregates in concrete involves the incorporation of recycled aggregates from CDW. However, challenges persist, with significant quantities of CDW in North Macedonia ending up in landfills or illegal dumps. Addressing these issues is crucial, particularly as CDW generation is expected to rise alongside economic development, exacerbating waste management challenges.
The primary goals of the project encompass exploring alternative binders with minimal CO_2 emissions to supplant Portland cement in concrete production, utilizing industrial waste by-products, and substituting natural aggregates in concrete with recycled aggregates sourced from construction waste. As industrial by-product, fly ash (derived from the combustion process in the REK Bitola thermal power plant in the Republic of North Macedonia) was used. Throughout the exchanged visits, international cooperation was established between TU Wien (Vienna, Austria) and Ss. Cyril and Methodius University (Skopje, North Macedonia). During

these visits, partners familiarized themselves with laboratory capacities and equipment. Working meetings were held to discuss project results and plan the next steps required for successful project realization. Additionally, opportunities for expanding cooperation and joint participation in scientific research projects were explored.

Project results expected from the project proposal

1. Determination of the physico-chemical characteristics of coal ash;

2. Determination of the physico-chemical characteristics of construction waste;

3. To define and optimize the process of alkaline activation for all process variables on which the activation will depend, such as: ash content, concentration of the activation solution, solid/liquid ratio, mixing time, amount of aggregate, care conditions, etc.;

4. Characterization of the obtained composites;

5. Data analysis.

Evaluation of the research results towards attaining the stated objectives and anticipated outcomes as detailed in the project proposal

Regarding the set goals contained in the project, it can be stated that they have been realized and are in close correlation with the expected results. In addition to the research, a characterization of the fly ash from the thermal power plant REK Bitola by determining the physico-chemical properties. The construction waste has been collected and separated. The physico-chemical properties of the selected samples were determined, from which their further application as aggregates derives.

The conditions for the preparatory procedures for obtaining the alkaline activated materials have been defined. The obtained composites showed comparable mechanical properties to these of the alkali-activated materials published in the literature.

Also, the fact that the results of the research have been presented at two international conferences, and one paper has been published in the proceedings of an international scientific conference, also supports the justification of the research.

Detailed report on the scientific research of the project

The project began with a comprehensive literature review covering current advances in alkali-activated materials and providing an overview of the volumes of waste dumped in North Macedonia. Task activities were then initiated. The first step involved collecting coal ash samples from the REK Bitola thermal power plant in the southwest of the Republic of North Macedonia for further analysis (see Figure 1).

Figure 1. - Fly ash landfill

Once the fly ash was retrieved from the landfill, it underwent separation and preparation for laboratory investigation, as depicted in Figure 2.

Figure 2. - Preparation of the fly ash material

Simultaneously with the collection of fly ash samples, samples were also gathered from construction waste (Figure 3) to serve as aggregate replacements in the matrices.

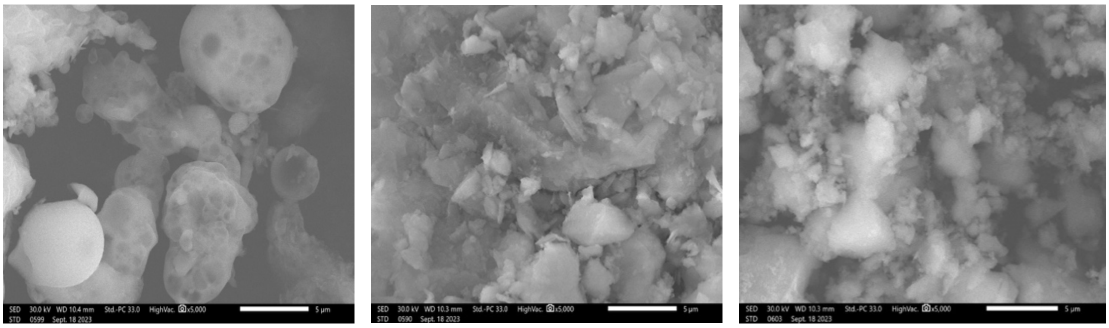
Figure 3. - Construction and demolition waste

The further tasks encompassed the following activities: sampling from nearby construction waste sites, processing brick waste material through crushing, grinding, and sieving (as illustrated in Figure 4), and processing plaster waste material through similar procedures of crushing, grinding, and sieving (as illustrated in in Figure 5). Subsequently, both materials were readied for further analysis.

Figure 4. – Preparation the brick waste material

Figure 5. – Preparation the plaster waste material

The prepered solid materials firstly underwent the microstructural analysis and their morphology was analyzed by scanning electron microscopy (SEM JEOL, JSM-IT200). The obtained SEM photos are presented in the Figure 6.

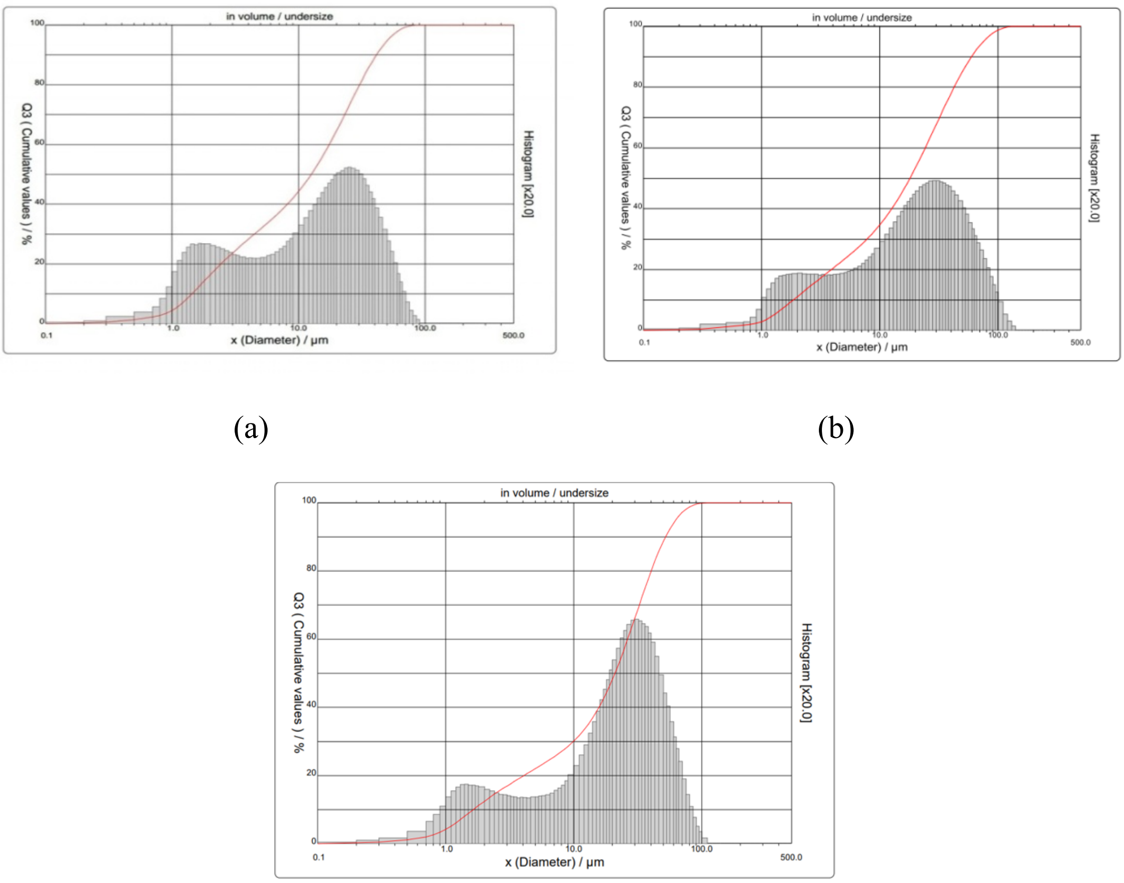


(a) (b) (c)

Figure 6. - SEM photos of the examined materials, x5000, bar 5mm; (a)-fly ash; (b)- brick waste; (c)- plaster waste

Figure 6 illustrates the morphology of various particles. In Figure 6a, particles from fly ash appear predominantly spherical with varying diameters. Additionally, aggregates and particles with undefined geometry are evident, likely originating from unburned coal particles present in the ash. Conversely, brick waste (Figure 6b) and plaster waste (Figure 6c) exhibit particles characterized by sharp edges and irregular geometries.

After the microstructural analysis, their physical properties were analyzed. The results of the investigations of the granulometric composition of the materials, determined by laser granulometry using a Retsch AS200 instrument, are shown in Figure 7.



(a) (b)

(c)

Figure 7. - Granulometric composition of (a) fly ash; (b) brick waste; (c) plaster waste

From the investigations of the granulometric system, it can be seen that there is a bimodal dependence in all the investigated materials, and the value of D50 for fly ash, waste brick and waste plaster is 12.33, 17.99, 20.96 µm, respectively.

The specific gravity of the materials was obtained by the pycnometer method. The specific surface area is defined using the Brunauer-Emmett-Teller (BET) method. Presence of moisture is calculated through the equation: $\%mcwb = (mw\text{-}md/mw)\times 100$, where mcwb is the percentage of moisture and mw is the mass of wet ash and md is the mass of dry ash. These results are not presented in the report of the project.

After the microstructural and physical investigation of the solid materials were conducted, the chemical properties were analyzed. The chemical composition of the materials determined by X-ray Fluorescence (model ARL 9900) is shown in Table 1.

Table 1. Chemical composition and loss on ignition (LOI) of the investigated materials

Oxides [wt%]	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**K_2O**	**Na_2O**	**SO_3**	**MgO**	**LOI**	**Σ**
fly ash	58.79	13.60	9.28	3.59	2.51	3.83	0.18	1.72	5.79	99.11
brick waste	61.12	17.58	8.45	7.82	0.29	0.33	/	3.01	0.86	99.64
plaster waste	38.5	5.59	3.18	27.37	0.16	0.17	0.41	3.31	20.54	99.23

The quantity of unburned coal was assessed by determining the LOI, achieved by heating a dry sample for two hours at 900 ºC. The chemical analysis revealed typical oxides present: SiO_2 and Al_2O_3, along with lesser amounts of CaO, MgO, Na_2O, K_2O, accompanied by 9.28 wt.% Fe_2O_3. The higher CaO content (7.82 wt. % in brick waste and 27.37 wt. % in plaster waste) is attributed to the presence of cement in the waste material, while the elevated LOI in the ash (5.79 wt. %) originates from unburned coal residues. These three chosen materials exhibit potential as aluminosilicate precursors due to their SiO_2 and Al_2O_3 content, essential for alkaline activation.

The final mixture design employed in the research began with the initial mixing of natural aggregate with two distinct waste aggregates - brick and plaster waste. The weight of the waste aggregates accounted for up to 50% of the total aggregate waste (including both natural and waste aggregates). Following this, fly ash was incorporated at a dosage of 50-100wt%. Subsequently, after adding the alkali activator, specimens were prepared for physical and mechanical testing (Figure 8).

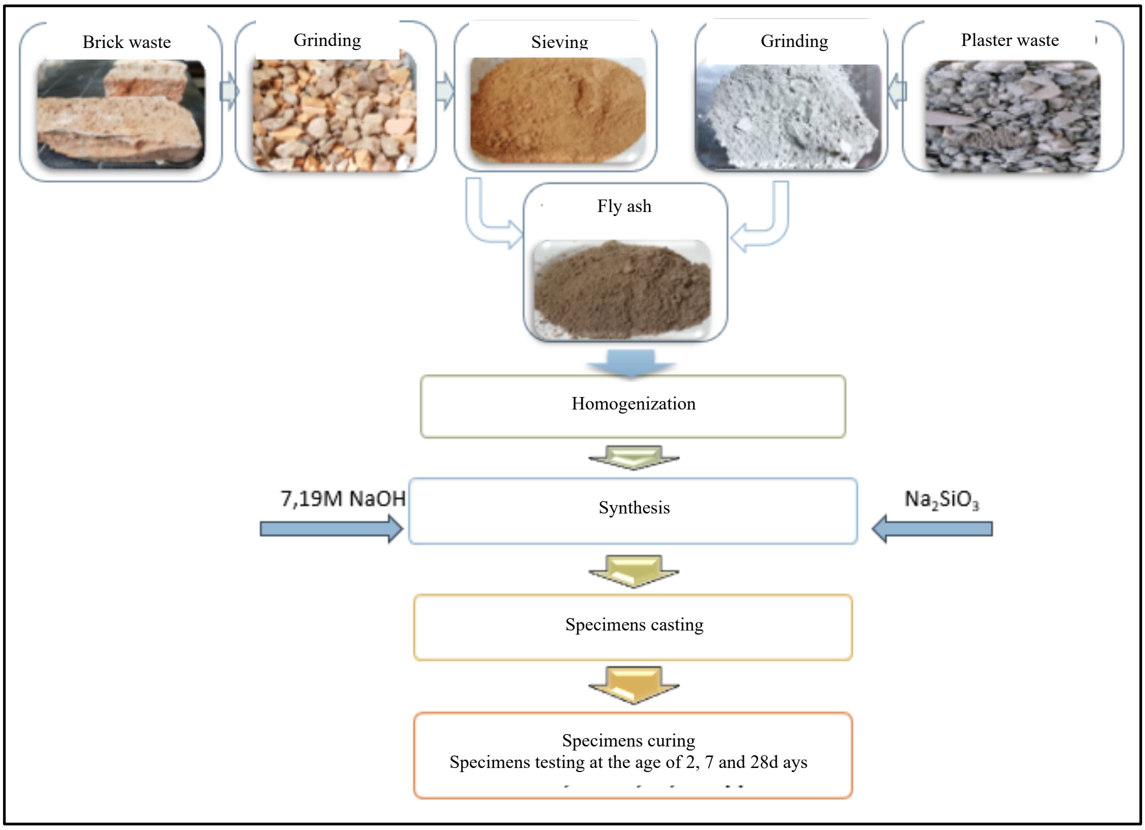


Figure 8. - Schematic representation of the synthesis of alkali-activated materials

The specimens were cast in the cubic molds 40x40x40mm^3, as illustrated in Figure 9 and Figure 10.

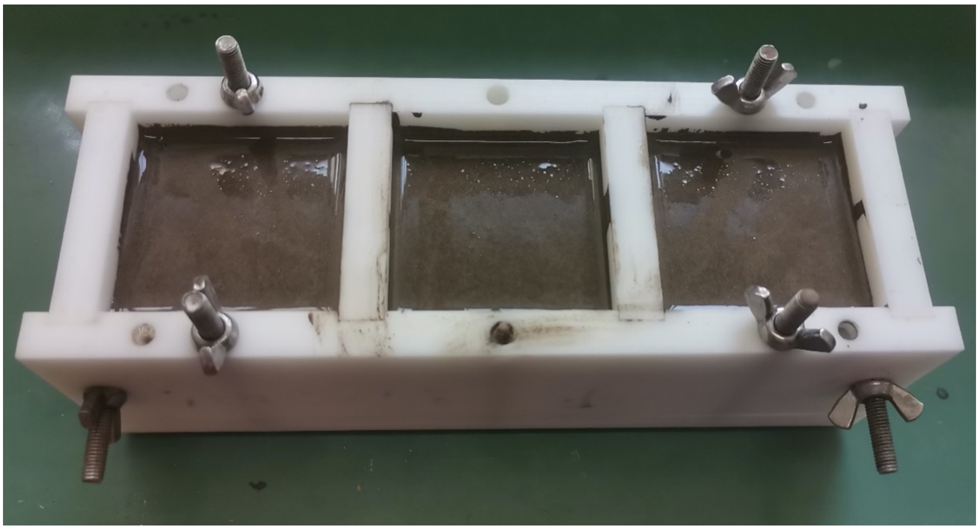


Figure 9. - Alkaline activation sample mold

Figure 10. - Samples of alkaline activated materials

The physical and mechanical properties of the specimens were examined at the ages of 2, 7, and 28 days. Dry test density, open porosity, and water absorption were assessed for physical properties, while compressive tests were conducted to analyze mechanical properties. Table 2 displays some of the obtained results.

Table 2. Compressive strength of alkaline activated materials after 7, and 28 days.

Sample	**AAM (CFA)**	**AAM co 10% brick waste**	**AAM co 20% brick waste**	**AAM co 50% brick waste**	**AAM (CFA)**	**AAM co 10% brick waste**	**AAM co 20% brick waste**	**AAMco 50% brick waste**
Curing time	7	7	7	7	28	28	28	28
s [MPa]	18.2	22.3	18.34	12.14	23.7	34.5	21.4	16.5

Overall, the compressive strength of all samples tends to increase as the curing time progresses. Samples with 50 wt% brick waste content in alkali-activated materials (AAFA50B) exhibit lower compressive strength values of 12.14 MPa and 16.5 MPa after 7 and 28 days of curing, respectively. Additionally, a noticeable trend is observed: higher fly ash content (lower brick waste content) correlates with higher compressive strength, likely attributed to the amorphous nature of the ash.

Further analysis was Fourier Transform Infrared Spectroscopy (FTIR). It's a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. It measures the intensity of infrared light absorbed by a material as a function of the frequency of the light, providing information about the chemical composition and structure of the sample.
Figures 11-13. show the results of the FTIR tests for some of the obtained alkali-activated materials.

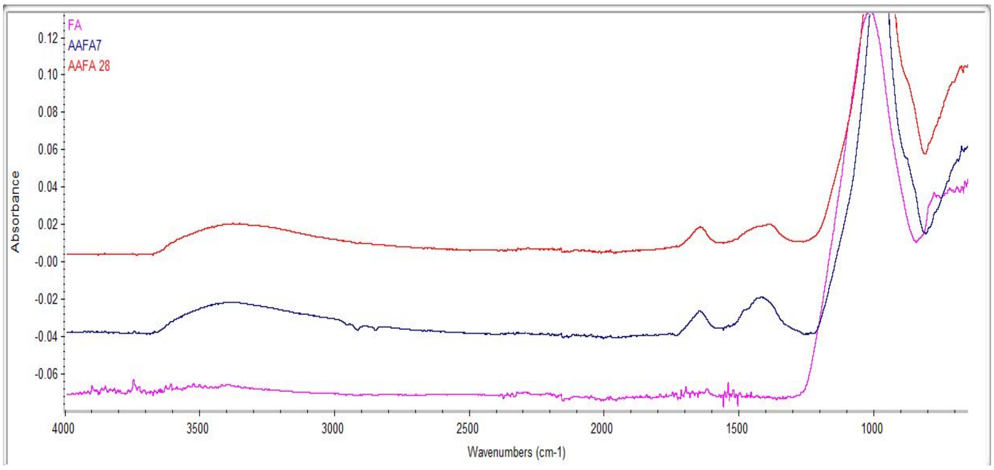


Figure 11. - FTIR spectrum of alkali activated fly ash

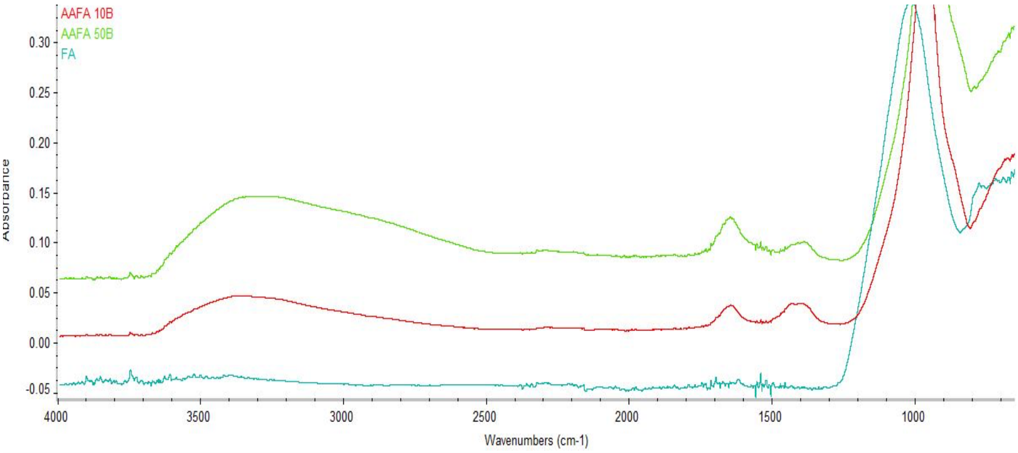


Figure 12. - FTIR spectrum of acyl-activated fly ash with addition of 10 and 50 wt% brick waste

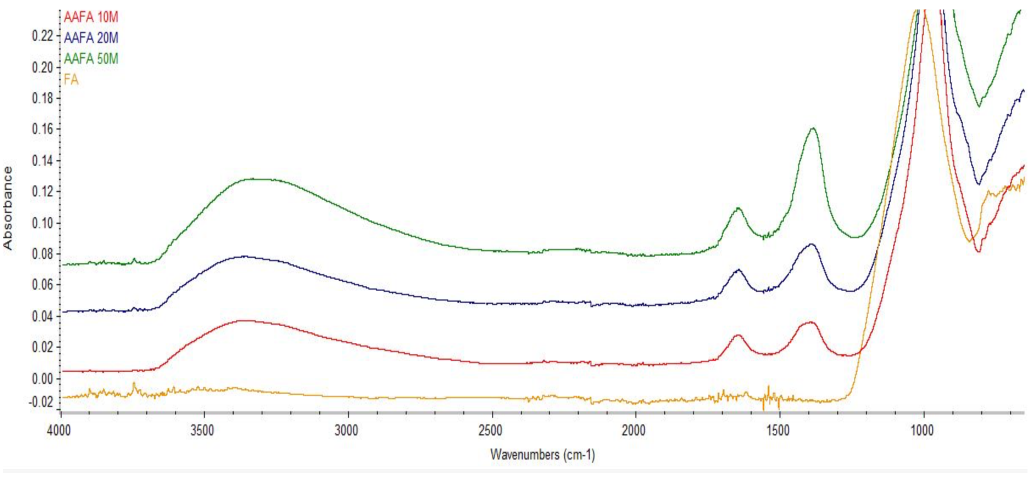
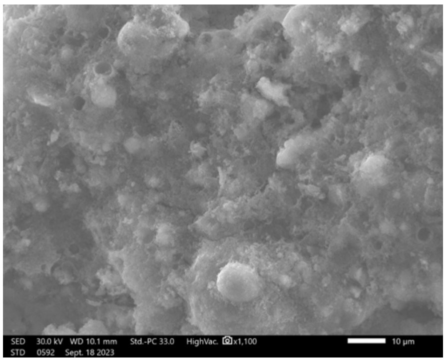
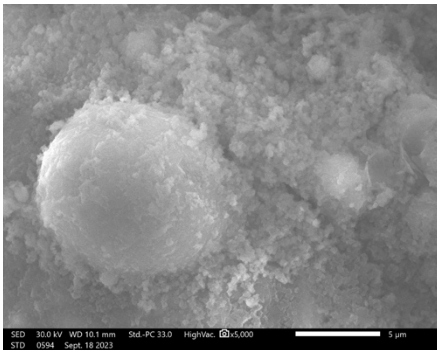


Figure 13. - FTIR spectrum of acyl-activated fly ash with addition of 10, 20 and 50 wt% WDM

FTIR spectra are mainly characterized by a broad peak in the region 3700-3100 cm^{-1} (O-H stretching vibration) and a peak around 1650 cm^{-1} (H-O-H bending vibration) in the spectrum of all alkali-activated materials which is correlated with the water present in the samples. The silicate structure characterized by a basic peak located at 1000 cm^{-1} is related to the Si-O-T stretching vibration (T=Si, Al), while the vibration at 1400 cm^{-1} is characteristic of $[CO_3]2-$ ions indicating carbonation.

Figure 14 shows the results of the investigations of the microstructure of the alkaline activated materials, as the last test conducted during the project investigation.





(a) **(b)**

Figure 14. - SEM micrographs of a sample of alkali-activated fly ash with 10% added WDB (AAFA10B), after 28 days a) x1000 bar 10mm, b) x5000 bar 5mm

SEM micrographs (Figure 14) show a recognizable fly ash morphology, gel-coated spherical particles, as well as closed spherical pores likely formed as a result of air entrapment during slurry mixing.

Summary of the research achieved results

Alkali activation, a process that transforms industrial by-products such as coal fly ash and construction and demolition waste into viable construction materials, is a promising solution towards sustainable practicies in the construstion industry. This study suggesst the synthesis of alkali activated materials from fly ash and construction and demolition waste as alumosilicate precusors while water glass and sodium hydroxide was used for preparation of the activation solution. The characterization of raw material was performed from chemical and physical aspects while alkali activated materials was studied by Fourier transform infrared spectroscopy, and Scanning electron microscopy . The compressive strength of the alkali activated materials vares from 3 to 14 MPa, depending on the fly ash and construction and demolition waste ratio and the solid/liquid content.

Significant scientific output obtained during the project

Through the analyses conducted during the project's implementation, it has been established that alkaline activation of industrial and construction waste by-products can yield materials suitable for construction applications. This achievement fulfills the dual objectives of the project: firstly, the utilization of industrial waste materials, thereby conserving natural resources; and secondly, the potential to substitute cement, a traditional binding material known for its high energy consumption and consequent CO_2 emissions during production. The researches of new alkaline activated materials are significantly present in the scientific community. Despite the fact of intensive research in this field, there is a lack of data on wider commercial production of the same, probably due to several socio-economic reasons. In addition to economic and commercial benefits, which include the production of potential building materials with a relatively lower cost resulting from the availability and cost of the initial materials as well as the obtaining procedure itself, there are also huge benefits in terms of environmental protection by preserving natural resources, such as and the possibility of replacing cement, the production of which is associated with high CO_2 emissions due to high energy consumption. Additionally, a significant outcome of the project is the mutual exchange of expertise between teams, laying the groundwork for potential future collaborations. In the Figure 15. the team visits of the partner insitute are presented. Both teams were also involved in the following conferences, where the project was disseminated and its outcomes were discussed: 5th International Conference on Bio-Based Building Materials, held from June 21st to 23rd, 2023, in Vienna, Austria. 26th Congress of SCTM, held from September 20th to 23rd, 2023, in Ohrid, Republic of North Macedonia (Figure 16). International Scientific and Professional Conference POLITEHNIKA 2023, held on December 15th, 2023, in Belgrade, Serbia.

(a) **(b)**

Figure 15. – Team TU Wien visiting team Ss. Cyril and Methodius University (a); Team Ss. Cyril and Methodius University visiting team TU Wien

Figure 16. – TU Wien team (Prof. Merta) together with team Ss. Cyril and Methodius University participating at 26th Congress of SCTM