Optimisation of Fly Ash Pretreatment for Mechanical Strength and Radioactive Safety in Microwave-Irradiated Alkali-Activated Materials: Preliminary Results

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The construction sector is a major contributor to global carbon emissions, due largely to high-temperature processing and extensive use of raw materials. Alkali-activated materials (AAMs), synthesised below 100 °C from secondary raw materials such as fly ash (FA), offer a more sustainable solution. This study investigates the mechanical performance and radionuclide presence of theoretically chemically optimal alkali-activated FA, based on three conditions: untreated FA, FA sieved below 200 µm, and FA treated thermally at 550 °C. Both the sieving and thermal treatment removed the organic content from the FA, resulting in a significant improvement in the compressive strength of the AAMs. However, in the absence of organic content, microwave irradiation no longer improved the compressive strength. Additionally, sieving below 200 µm also reduced the radionuclide content, offering a simple and effective pathway to high-performance, radwaste-safe building materials, even though the radionuclides themselves did not affect the mechanical performance of the AAM.

Keywords:
alkali-activated materials,
radioactive fly ash,
naturally occurring
radioactive material,
radionuclide separation,
microwave irradiation,
circular economy

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1 Introduction

The building and civil engineering industry has a significant impact on the environment, by contributing over 40% of human-made carbon emissions (The Industry Creating a Third of the World's Waste, n.d.). This is a consequence of the use of large quantities of raw materials, which account for almost two-thirds of the mass of Mount Everest per year (The Industry Creating a Third of the World's Waste, n.d.), and processing at temperatures exceeding 1000 °C (Cement Production: How Hot Air Becomes Green Energy, n.d.). To reduce the environmental concerns, the building industry is exploring alternative materials, such as alkali-activated materials (AAMs) with synthesis temperatures below 100 °C and secondary raw materials as reagents, which can even transform the built environment from a net carbon emitter into a carbon sink (Škvára, 2007).

Potential precursors for alkali activation are inorganic materials rich in amorphous Al and Si, such as fly ash (FA). Although FA is one of the most researched materials for alkali activation, its main disadvantages (e.g., cellulose and radionuclide content) have not yet been explored sufficiently.

The amount of cellulose in the FA is related directly to the completeness of coal combustion: the more incomplete the combustion, the more organic residues remain in the ash. In contrast to wood used in construction, where cellulose is protected from degradation deliberately through structural design and chemical treatments, the cellulose found in FA is only encapsulated randomly by the surrounding inorganic material of the AAM. The uncontrolled encapsulation may be ineffective, or even detrimental to the long-term durability of the AAMs, as cellulose is prone to degradation. In addition, the FA contains concentrated naturally occurring radioactive materials (NORM), originating from the coal itself. While alkali activation can immobilise radionuclides within a stable aluminosilicate matrix, this entrapment may not be sufficient in cases where the FA exhibits elevated levels of radioactivity, such as the material investigated in this study.

Therefore, this preliminary study aimed to remove the cellulose by mechanical and thermal treatment, while assessing how these treatments affect the radionuclide content in the FA. To evaluate the effect of FA treatment on the AAM performance, the compressive strength was compared to the AAM produced from the as-received FA, which was used as a reference.

2 Experimental

2.1 Materials and characterisation of the materials

In alkali-activated synthesis, only two ingredients were used- a precursor and a liquid alkali:

- The precursor used for alkali activation was Slovenian FA from the Slovenian Thermal power plant, which is known for its high radionuclide content, which exceeds the regulatory limits for use in construction (Fidanchevski et al., 2024). Therefore, this material cannot currently be reused as part of the circular economy and is classified as 100% waste.
- The alkali component used with the FA was an Na-silicate solution (Geosil, 344/7, Woelner, 16.9 $m_{\%}$ Na_2O, 27.5 $m_{\%}$ SiO_2, 55.6 $m_{\%}$ H_2O), which was used as an aqueous liquid alkali without further manipulation.

The FA was characterised using several complementary techniques:

- Loss on ignition (LOI), performed at 550 °C for 2 h, was used to determine the organic content in the FA,
- X-ray fluorescence (XRF, Thermo Scientific ARL Perform'X Sequential XRF) was used to determine the chemical composition, which includes chemical elements from fluorine to americium. For the XRF analysis, the samples were milled and sieved below 125 μm, and then treated thermally at 950 °C for 2 h.
- X-ray diffraction (XRD, Empyrean PANalytical X-ray Diffractometer, Cu X-Ray source) was used to determine the minerals present in the FA. The samples were milled and sieved below 125 μm, placed in XRD sample holders, and measured under clean room conditions in the 2θ range from 4 to 70° and a step size of 0.0263°.
  The Rietveld refinement of the XRD spectra was performed using the X'Pert Highscore plus 4.1 software and an external standard (corundum, Al_2O_3) to quantify the crystalline content. The amorphous content in the FA was

calculated as the element-wise difference between the XRF and XRD (per element, not per oxide). The summary of the XRF and XRD characterisation results is presented in Table 1, while the raw data are stored in the open repository.

Table 1: Mass percentage ($m_{\%}$) of crucial elements in the alkali activation.

Elements [$m_{\%}$]	Na	K	Mg	Ca	Al	Si	Content [$m_{\%}$]
XRF (whole material)	0.68	2.04	1.53	6.34	14.08	20.40	100.0
XRD (crystalline)	0.00	0.00	0.57	0.94	3.15	4.36	25.1
Amorphous	0.68	2.04	0.96	5.40	10.93	16.04	74.9

To obtain cellulose-free FA for the alkali-activated synthesis, different processing methods were applied to the original FA:

- sieving below 200 µm, between 200 and 400 µm, and above 400 µm, and
- thermal treatment at 550 °C for 2 h at a heating rate of 10 °C/min, followed by natural cooling inside the furnace to room temperature.

The efficiency of the organic content removal in the sieved sample was assessed in the same way as for the as-received FA, namely, by determining the LOI at 550 °C. In parallel, the chemical composition was analysed by XRF spectroscopy, to monitor the presence of radionuclide-related elements that can be detected by the used XRF apparatus.

Only the mechanical properties (compressive strength, bending strength and geometric density) were evaluated in this preliminary study. All the measurements were performed on 3-day-old AAMs using a ToniTechnik ToniNORM testing machine.

2.2 Synthesis of the material

The mixture of FA and alkali solution was pre-calculated using the XRF and XRD results of the original FA, excluding the organic content. The precalculation was performed under boundary conditions, with the aim that for the molar ratio of amorphous:

– Si to Al should be 1.9 to 1 to achieve the highest compressive strength,
– Al to the sum of the chemical elements from the 1st group of the periodic table 1 to 1, or even 1 to <1, to avoid efflorescence and degradation of the AAM.

The theoretically determined mass ratio (using software designed in the MS Excel platform, developed in project no. C3330-17-529032 "Raziskovalci-2.0-ZAG-529032" (Horvat & Ducman, 2019) and upgraded in the ARIS project under Grant no. J2-3035) between the FA and liquid alkali was 1:0.35.

Three mixtures, with the same mass ratio of precursor and alkali (1:0.35, respectively), were prepared using: a) as-received FA, b) FA with the lowest cellulose content (sieved below 200 µm), and c) FA treated thermally at 550 °C for 2 h, as shown in Figure 1.

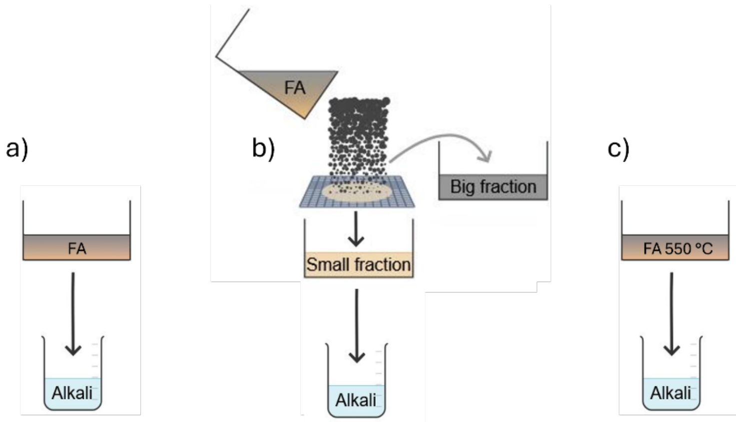

Figure 1: Synthesis scheme.
Source: own.

The precursor and the alkali were mixed for 2 minutes at up to 1,000 rpm. The resulting slurry was then moulded into silicone rubber moulds, each containing 6 prisms (2 × 2 × 8 cm^3), and subjected to one of the following curing procedures:

– Microwave-assisted curing: The mould with only one prism was exposed to low-power microwave irradiation (100 W, inverter microwave oven Panasonic, NN-CD575M, frequency 2.45 GHz, magnetron source) for 2 minutes to induce volumetric heating, promote dissolution and enhance the reaction kinetics throughout the slurry. The prism was positioned at the 1st observed dosimetry maxima position (~6 cm from the centre of the turntable) (Horvat et al., 2024). After irradiation, the prism remained in the mould, and was cured under conventional conditions at 70 °C for 60 hours.

– Conventional curing: The remaining prisms were cured without microwave treatment, under the same conventional conditions (60 h at 70 °C).

3 Results and discussion

The XRF results for the minor elements, expressed as oxides, together with the LOI values determined at 550 °C, are summarised in Table 2 for the as-received FA and the sieved fractions. Since the thermal treatment at 550 °C does not affect the overall chemical composition of the inorganic content of the FA, and the samples were already pre-treated at 950 °C for XRF analysis, no additional XRF was performed for the thermally treated FA. Namely, its chemical profile was considered to be equivalent to the as-received FA. The changes caused by the thermal treatment are expected at the mineralogical level, but not in the elemental composition.

Although the total organic content in the FA is less than 1 m%, it was not distributed uniformly across the particle size distribution. The largest fractions of FA contain the highest concentration of organic content: (i) the fraction between 200 and 400 μm contained more than 5 $m_{\%}$, and (ii) the fraction above 400 μm contained more than 20 $m_{\%}$.

Because the concentration of radionuclide was above the detection limit of XRF, the radionuclide elements were measured both in the as-received FA and in the coarsest fractions (between 200 and 400 μm, and above 400 μm). However, the presence of radionuclide elements was below the detection limit in the fraction below 200 μm.

Therefore, the fraction below 200 μm was selected as the main sample, as it contained a minimal organic content and no detectable radionuclides based on the XRF analysis.

Table 2: XRF results for minor elements and LOI performed at 550 °C.

Oxides [10^{-2} $m_{\%}$]	CuO	Ga_2O_3	Nb_2O_5	Ag_2O	PbO	ThO_2	PuO_2	LOI 550°C
FA	0.44				0.65		0.52	0.70
FA < 200 µm				1.52				0.62
FA 200 – 400 µm		0.33	0.33			1.07		5.50
FA > 400 µm			0.48				0.66	21.49

The mechanical strengths of the non-irradiated samples are shown in Figure 2, the comparison between irradiated and non-irradiated samples in Figure 3, and their geometric densities in Figures 4 and 5.

The bending strength was below 5 MPa for all the samples, which was to be expected given the absence of fibre material that would increase the flexural resistance. The highest bending strength was observed in the sample prepared from the FA treated thermally at 550 °C. This sample also exhibited the highest geometric density, which is consistent with the effective thermal removal of the organic content. However, the compressive strength, which was already high (46 MPa) for the AAM prepared from the as-received FA, increased further when the cellulose was removed from the precursor, regardless of the procedure (sieving or thermal treatment), reaching up to 62 MPa. Therefore, sieving is considered to be the more favourable method, as it requires significantly less energy for sample preparation, and results in a lower carbon footprint of the final material.

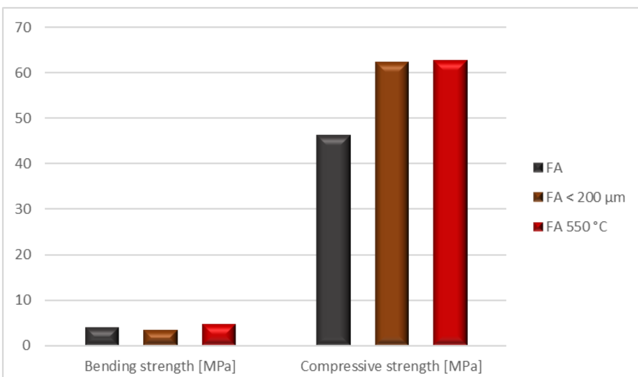

Figure 2: Bending and compressive strength of the non-irradiated samples prepared from the as-received FA, FA sieved below 200 µm, and FA treated thermally at 550 °C.
Source: own.

The experimental results presented in Figure 3 show that the low-power microwave irradiation improved the mechanical properties of the AAM synthesised from the as-received FA. In contrast, no such improvement was observed for the sample prepared from the FA sieved below 200 µm, as the cellulose had already been removed, as well as the radionuclides detectable by XRF.

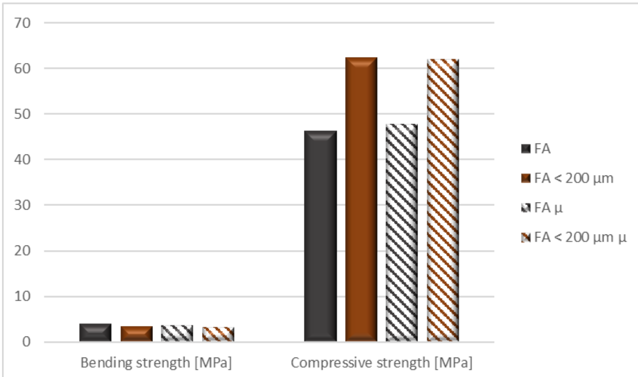

Figure 3: Bending and compressive strength of the non-irradiated and irradiated samples prepared from the as-received FA and the FA sieved below 200 µm.
Source: own.

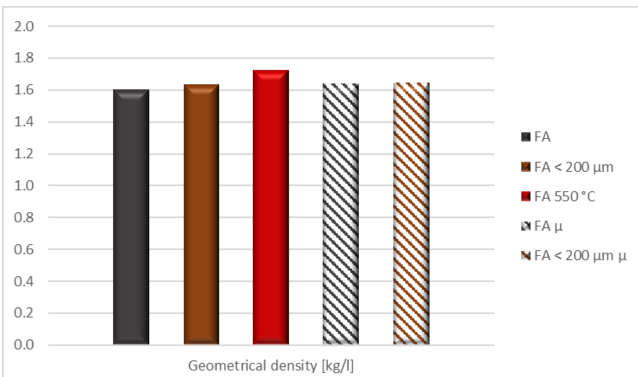

Figure 4: Geometric density of the non-irradiated and irradiated samples prepared from the as-received FA, FA sieved below 200 µm, and the FA treated thermally at 550 °C.
Source: own.

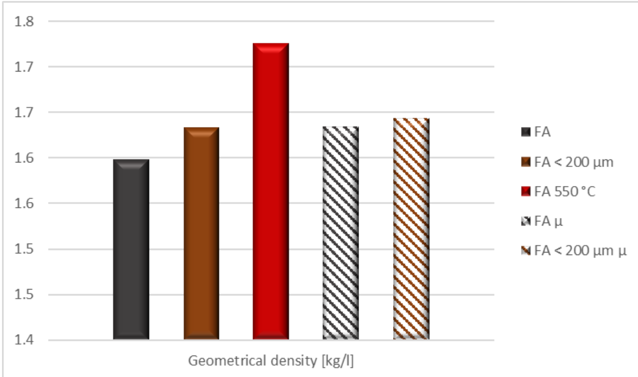

Figure 5: Cut y-axis (for easier comparison of the values) of the geometric density of the non-irradiated and irradiated samples prepared from the as-received FA, FA sieved below 200 µm, and the FA treated thermally at 550 °C.

Source: own.

This suggests that the observed increase in strength after irradiation was due either to thermal degradation of the cellulose present in the as-received FA, or to improved dissolution of the surrounding inorganic material due to localised heating near the cellulose particles. Although the cellulose content was less than 1 m%, the compressive strength increased by 2 MPa after irradiation. However, the intentional addition of cellulose to the FA would probably not lead to a significantly higher increase in compressive strength after irradiation, as the cellulose itself does not contribute to the mechanical performance of the inorganic AAM matrix, and would most likely reduce the compressive strength (Pavlin et al., 2022). Indeed, the samples with removed cellulose had 16 MPa higher compressive strength than the samples with cellulose.

Nevertheless, the presence of radionuclides had no observable impact on the mechanical behaviour of the AAM, as their concentrations were too low to influence the bulk-scale properties.

4 Conclusion

This study has shown that even a small amount of cellulose affects the mechanical performance of AAMs negatively, and that their removal, particularly by sieving, is an efficient, cost-effective, energy-saving, environmentally friendly and low-carbon solution. While the separation of radionuclide needs further validation, the addition of a sieve represents a viable pathway for the development of high-performance, environmentally sustainable and radwaste-safe construction materials.

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Data availability status

The original data presented in the study are openly available in the repository Zenodo at https://zenodo.org/records/16531514 with DOI: 10.5281/zenodo.16531514.

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Barbara Horvat, PhD, is a physicist and project leader at the High Voltage and Power Plants Department, in the nuclear group. Her research focuses on radioactive waste (management), (green) building materials, (electrical and thermal) insulation materials, especially fire-resistant electrical cables, semiconductors, the circular economy in material science, and life cycle assessment (LCA). She earned her BSc in Physics with a thesis on eye-safe LIDAR for aerosol detection and her PhD in Nanophysics, studying photocatalytic degradation of organics using TiO_2 nanoparticles. Her postdoc involved chemical and mineralogical evaluation of primary and secondary raw materials for alkali-activated materials, including software development for recipe optimisation using XRF/XRD. She led teams to multiple circular economy awards for inventions, especially connected with the influence of the electromagnetic field on new materials.

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Lara Petrič, BSc student, is studying at the Biotechnical Faculty, University of Ljubljana. As part of a summer research internship, she contributed to the synthesis and characterisation of alkali-activated materials within the ARIS project, including sample preparation, mechanical testing, and chemical and crystallographic analyses. As a promising student, she has also begun contributing to abstracts and presentations for scientific conferences.

Sara Tominc, PhD, is a chemist at the Department of Materials, in the Laboratory for Cements, Mortars and Ceramics, at the Slovenian National Building and Civil Engineering Institute. Her research focuses on traditional ceramics and on the beneficial use of waste materials in the construction industry. She earned her BSc in Chemistry and Chemical Engineering at the University of Maribor and her PhD at the Jožef Stefan Institute, investigating the influence of pentavalent dopants on twinning and microstructure development in SnO_2 ceramics for high-performance varistors and dielectrics. She specialises in electron microscopy, thermal analysis and waste characterisation. Recently, she has been investigating accelerated mineral carbonation, aiming to understand the mechanisms and kinetics of CO_2 sequestration and to optimise carbonation conditions.

Summary

The study investigates the optimisation of fly ash (FA) pretreatment for producing alkali-activated materials (AAMs) with high mechanical strength and reduced radioactive content. Three FA conditions were compared: as-received, sieved below 200 μm, and treated thermally at 550 °C. Both the sieving and thermal treatment removed the residual cellulose effectively, enhancing the compressive strength significantly, while the microwave irradiation improved the strength only in the as-received FA containing organic content. Sieving below 200 μm also reduced the detectable radionuclides, providing a simple, energy-efficient and low-carbon approach to synthesising high-performance, radwaste-safe AAMs. The preliminary results highlight sieving as a promising method to produce environmentally sustainable construction materials from radioactive FA.