

Hydration and Carbonation Behaviour of Selected Recycled Materials from Slovenia

DIM-ESEE Conference

Vesna Zalar Serjun^{1*} , Primož Oprčkal¹ , Anton Meden² 
Marta Počkaj² , Romana Cerc Korošec² 



¹ Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, SI-1000 Ljubljana, Slovenia) ²Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

Abstract

The European Union's shift towards a circular economy emphasizes the substitution of virgin materials with recycled alternatives, particularly in the construction sector, which can accommodate large volumes of industrial by-products. Ashes from coal, biomass, paper sludge, and co-combustion processes are abundant secondary materials whose variable chemical and mineralogical compositions necessitate careful assessment to enable safe and effective reuse.

This study investigates the hydration behaviour and early carbonation potential of ashes of different origin. The ashes were characterized using X-ray fluorescence, X-ray diffraction, and scanning electron microscopy coupled with energy-dispersive spectroscopy. Hydraulic reactivity was evaluated by preparing ash pastes at a 1:1 water-to-ash ratio and monitoring hydration product formation over time using XRD. Carbonation of co-combustion ash was studied under controlled CO₂ conditions (2 % CO₂, 50 % RH, 20 °C ± 1 °C) at different moisture contents (0 wt.%, 10 wt.%, 20 wt.%, and 40 wt.%) and early curing times (0 hours, 1 hours, 4 hours, and 24 hours).

Results indicate distinct differences among the ashes. Paper sludge ash exhibited the most extensive formation of calcium aluminate hydrates, coal and co-combustion ashes showed moderate hydration, while biomass ash produced only minor secondary phases. Carbonation of co-combustion ash proceeded concurrently with hydration, with lime depletion and calcite formation enhanced by higher moisture and longer curing. These coupled processes influenced both the kinetics and composition of hydration products. The findings demonstrate the potential of diverse combustion ashes for valorisation in construction materials and provide insight into their reactivity under early-age hydration and carbonation conditions, supporting circular economy initiatives.

Keywords: Combustion ash, Hydration, Carbonation, Circular economy, Construction materials

1. Introduction

The European Union is transitioning from a linear to a circular economy to extend material lifecycles and reduce waste. The 2020 Circular Economy Action Plan, part of the European Green Deal, emphasizes replacing virgin resources with recycled alternatives (European Commission, 2020). With global waste generation projected to rise by 70 % by 2050, an estimated 600 million tonnes of waste-based materials could be reused annually (European Commission, 2008; European Commission, 2015). The construction sector is particularly well suited for repurposing industrial by-products such as ashes, which enable large-scale material reuse while stabilizing harmful elements. In support of this, the SIST EN 16907-2 (2020) standard, introduced in 2019, allows the use of processed and recycled materials in construction composites.

Ashes produced in air pollution control systems of industrial and energy processes differ according to fuel source and combustion method. As coal use declines, biomass and co-combustion ashes (e.g. from sewage sludge, biomass, or municipal solid wastes) are becoming more prevalent. Although most ashes are still disposed of, only a small proportion is currently recycled (Hogg, 2022). Their composition varies with fuel type, plant operations, and storage conditions, which affects reuse potential and requires case-specific evaluation (Singh et al., 2016; Zhao et al., 2017).

Previous studies (Yao et al., 2015; Wei et al., 2023; Ding et al., 2024; Aboustait et al., 2016) have highlighted ash applications in cement production, lightweight aggregates, backfill, panel boards, and soil treatment. Standardization remains critical for safe and effective use, yet most regulations focus on coal fly ash, with limited provisions for other ash types. Nevertheless, practical applications demonstrate that a wider range of ashes can enhance geotechnical performance, for example by stabilizing soils or immobilizing contaminants (Zalar Serjun, 2024).

Recent studies have expanded understanding of ash reactivity, hydration, and carbonation mechanisms. For example, Shi et al. (2025) investigated how the amorphous phase content of recycled fly ash influences hydration kinetics, showing that higher amorphous content accelerates reaction rates and improves binding properties. Skevi et al. (2022) demonstrated that mechanochemical pre-treatment and mineral carbonation of biomass bottom ash enhance its pozzolanic activity and improve strength development when used as a supplementary cementitious material. Similarly, a review by

*Corresponding author: Vesna Zalar Serjun
e-mail address: vesna.zalar@zag.si

Gupta et al. (2024) on coal bottom ash reported that optimal fineness and controlled replacement ratios can yield concrete with comparable mechanical and durability performance to conventional mixes.

In terms of carbonation, Pihlajavaara et al. (2023) reviewed accelerated mineral carbonation processes in cementitious materials and industrial by-products, emphasizing the role of moisture and reactive calcium phases in CO₂ uptake. Laboratory-scale research by Li et al. (2024) found that CO₂ uptake in hydrated cementitious systems can reach up to 70 % of the theoretical capacity within the first 40 minutes, highlighting the importance of early carbonation kinetics. Moreover, Rahman et al. (2025) assessed wastewater sludge ash as a cement substitute and reported that controlled carbonation can improve durability while immobilizing potentially hazardous elements.

Compared with these studies, our work focuses specifically on industrial by-products from combustion processes, assessing both their hydration behaviour and mineral carbonation potential at early curing stages. Several types of combustion ashes were hydrated, with curing monitored over time, while the carbonation capacity of co-combustion ash (wood chips added to coal during combustion) was evaluated under different moisture contents at early time intervals (up to 24 hours). This approach contributes to understanding the short-term reactivity and CO₂ sequestration potential of co-combustion ashes — a topic that remains underexplored in current literature.

2. Materials and Methods

Four different ashes from various incineration processes were investigated in this study, namely from coal, co-combustion, paper sludge and biomass incineration. Macroscopic appearance with the microstructure of investigated ashes is shown in **Figure 1**.

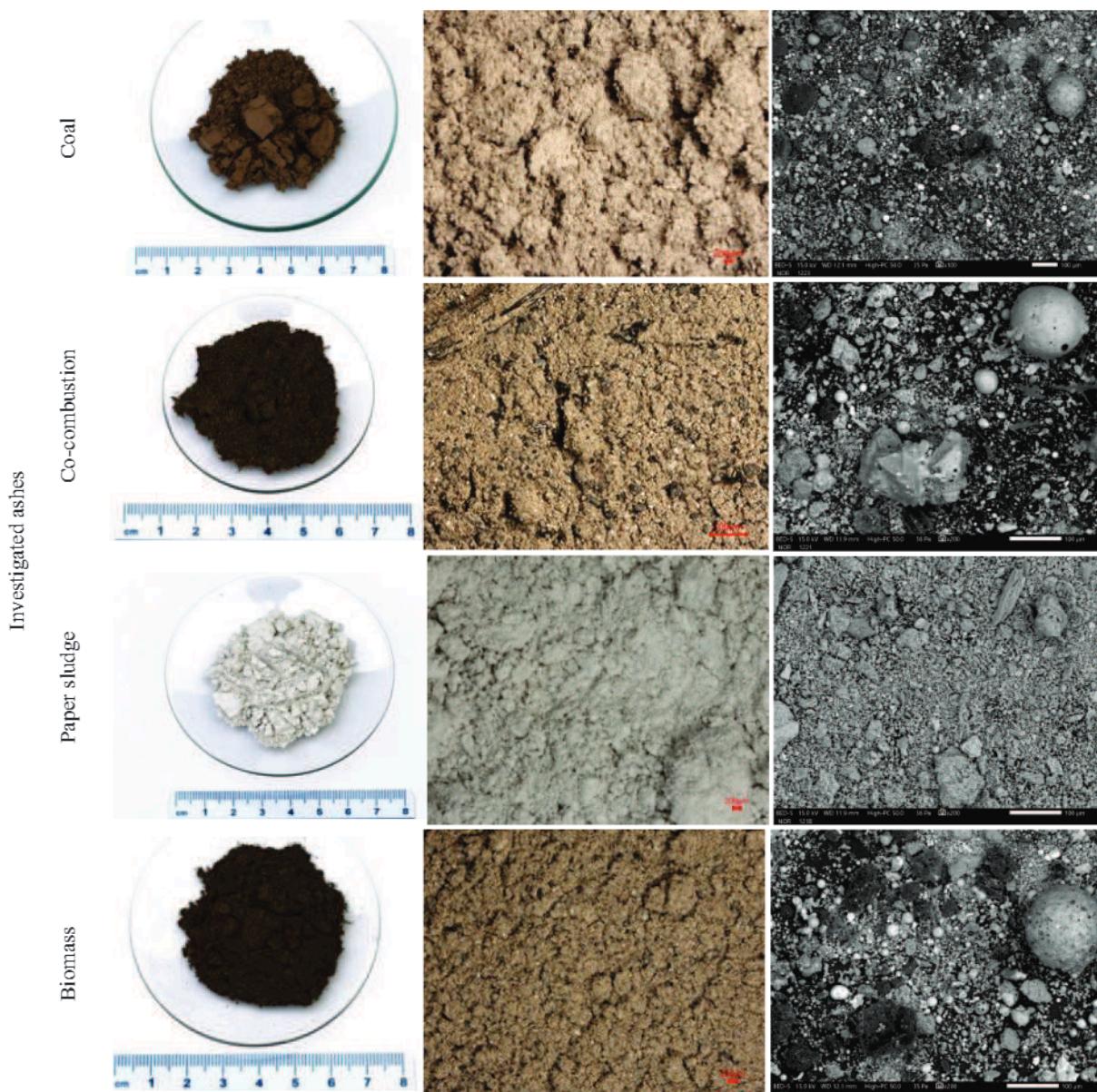


Figure 1. Investigated ashes

Ashes were characterized for their phase and chemical composition. Phase composition was determined using the quantitative powder X-ray diffraction (QXRD), using an Empyrean (PANalytical, Netherlands) diffractometer with Cu-K α radiation. Powder diffraction data were collected at a tube tension of 40 kV and a tube current of 45 mA using a 20 step size of 0.02° and measurement time of 100 s per step. Quantitative phase analysis was performed using the Rietveld refinement method, employing the external standard approach and the K-factor method. NIST alumina (corundum SRM 676a) was used as the external standard. Bulk chemical composition was analysed by X-ray fluorescence (XRF), using Perform-X ARL (Thermo Fischer, USA). The samples were prepared as glass disks. The sample-to-flux ratio was 1:10. The flux used for this study was 50 % lithium tetraborate with 50 % of lithium metaborate. The microstructural and mineralogical features were investigated further by scanning electron microscopy (SEM) using a JEOL JSM-IT500LV (Tokyo, Japan) microscope equipped with energy dispersive spectroscopy (EDS) (Oxford Instruments, UK).

To study the hydraulic reactivity, ash pastes were prepared by mixing ash with water at a 1:1 ratio. The formation of hydration products was monitored by XRD at selected time intervals.

The carbonation of co-combustion ash was investigated on a sample collected directly from the production process (rather than obtained through conventional process handling) to assess its maximum CO₂ sequestration capacity under varying moisture contents and controlled CO₂ levels at early-age time intervals of up to 24 hours (0 hours, 1 hours, 4 hours, and 24 hours). Water was admixed with ash at different contents (0 wt.%, 10 wt.%, 20 wt.%, and 40 wt.%), and the samples were conditioned in a CO₂ chamber under the following parameters: CO₂ = 2 %, RH = 50 %, and $T = 20.0\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

3. Results and Discussion

The results of the XRF analyse is shown in **Table 1** (according to Snellings et al., 2023).

The differentiation into four groups is determined by the fuel type used in combustion. Coal and co-combustion are characterized by silico-aluminous ashes with the lowest (earth) alkali contents, biomass ashes are characterized as more calcareous, whereas paper sludge combustion is characterized by ashes with the highest alkali concentrations.

The results of the QXRD analysis is shown in **Figure 2**. Coal ashes exhibit the highest proportion of amorphous phases, followed by co-combustion and biomass ashes, with paper ashes containing the least. In contrast, paper ashes are enriched in calcium-bearing phases, including calcite, portlandite, and lime. Apart from weakly hydraulically active phases such as gehlenite, no other well-defined cementitious phases were identified in investigated ashes.

Table 1. The results of the XRF bulk chemical composition

ASH	Chemical composition (wt.%)		
	CaO+MgO+Na ₂ O+K ₂ O	SiO ₂	Al ₂ O ₃ +Fe ₂ O ₃
Coal	14.4	47.9	34.6
Co-combustion	27.4	31.1	20.8
Paper sludge	46.9	12.2	13.3
Biomass	34.3	19.7	9.0

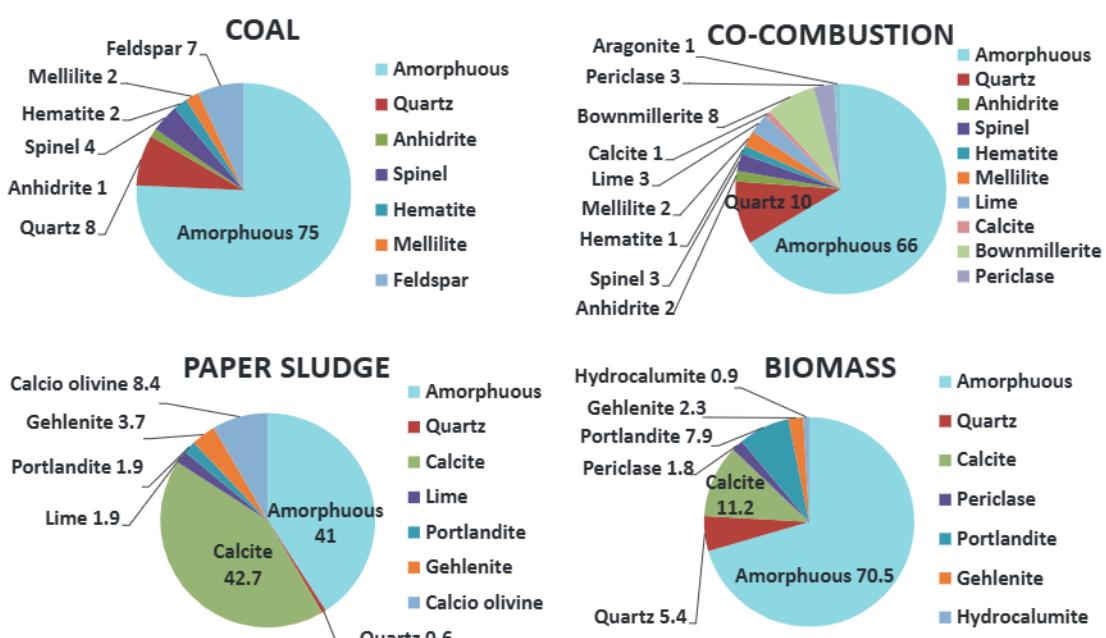


Figure 2. QXRD analysis of investigated ashes.

The morphology of grains composed of amorphous phases varies among the ashes. Coal and co-combustion ashes contain well-rounded spherules, whereas biomass and paper sludge ashes exhibit more irregularly shaped grains with rounded pores (Mohebbi et al., 2022, Oprčkal et al., 2020). In the latter, the amorphous phase is more finely interspersed with the fine-grained matrix, and spherules are absent. Amorphous grains are often highly heterogeneous, comprising different elements in varying ratios, making it difficult to define their overall composition for each ash type. Figure 3 illustrates various types of amorphous grains, together with EDS analyses (averaged from 20 measurements of amorphous grains per sample, taken from points like those designated as "x" in the illustration) for coal and paper sludge ashes. The results, expressed in atomic percentages (at.-%), show the maximum and minimum values of selected elements, highlighting the broad compositional variability of the amorphous phases.

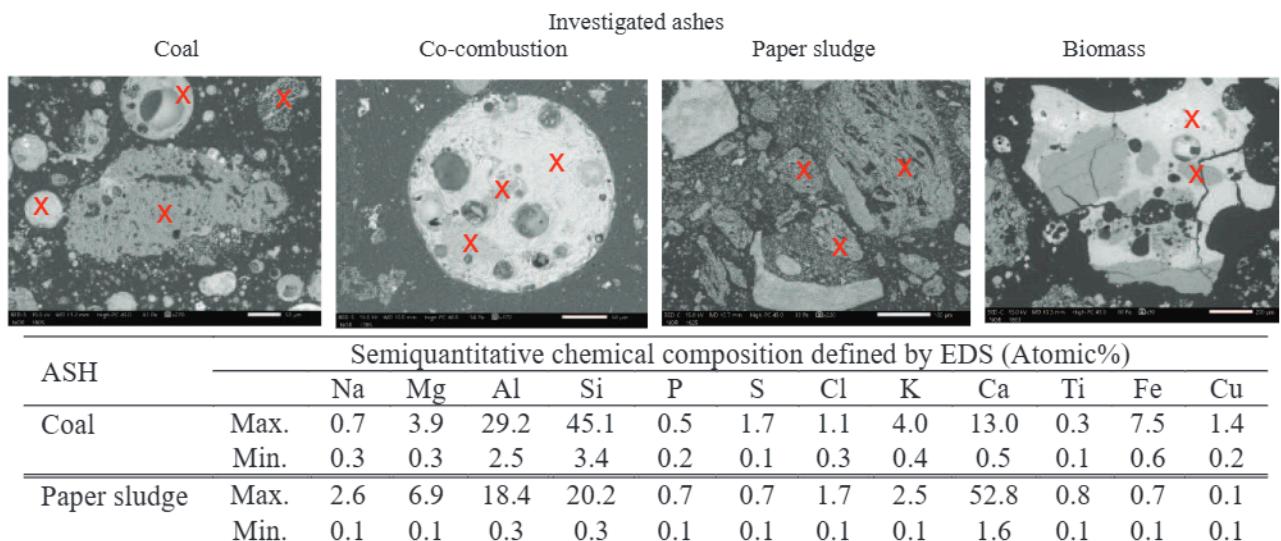


Figure 3. Variations in the appearance of amorphous phase grains among ashes

Time-resolved XRD analysis (2D, 7D, 14D, 28D, 56D, 90D, and 180D, corresponding to 2, 7, 14, 28, 56, 90, and 180 days) of ash paste hydration products (example of co-combustion ash shown in Figure 4) revealed the formation of various calcium aluminate hydrates (CAHs) characteristic of cementitious hydration, including Aft (ettringite) and AFm phases (hemicarboaluminate, monocarboaluminate and hydrocalumite). Paper ash pastes exhibited the most extensive formation of CAHs. In coal and co-combustion ash pastes, CAH development increased over time and was clearly detectable. In contrast, biomass ash pastes exhibited only minor amounts of newly formed phases.

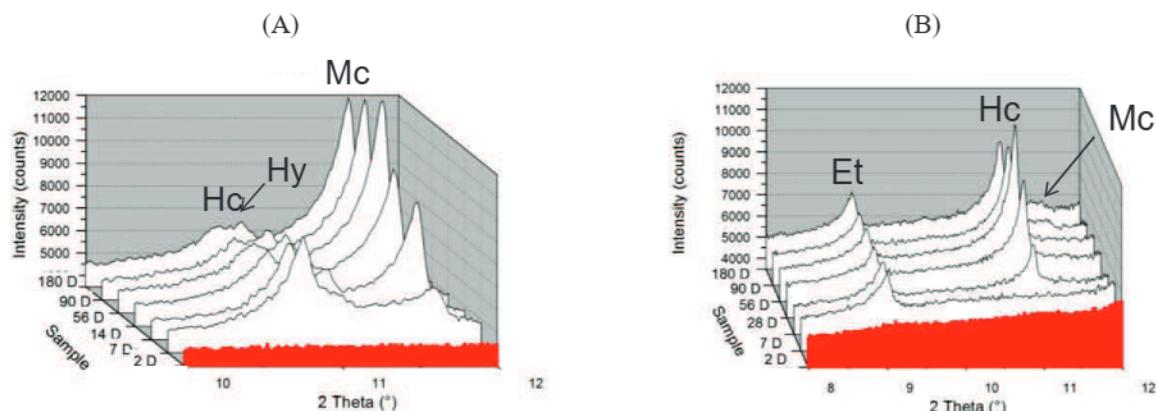


Figure 4. Time dependent XRD results of paper sludge (A) and co-combustion ash (B) pastes; Et- ettringite; Hc- hemicarboaluminate; Mc- monocarboaluminate; Hy- hydrocalumite

The results of the carbonation of co-combustion ash show a clear transition of lime into hydrated and carbonated forms (Figure 5), primarily calcite. Higher moisture content (wt.%) and longer curing times enhanced the carbonation process, confirming the positive carbonation potential of this ash. The findings also indicate that hydration and carbonation occur simultaneously and can influence one another. Their interaction under curing conditions is often complex. Hydration products such as $\text{Ca}(\text{OH})_2$, ettringite, and C-S-H are prone to carbonation, while the main carbonation product, CaCO_3 , can in turn affect both the kinetics of hydration and the composition of the hydration phases. A comprehensive understanding of these coupled processes is therefore essential for describing the hardening behaviour.

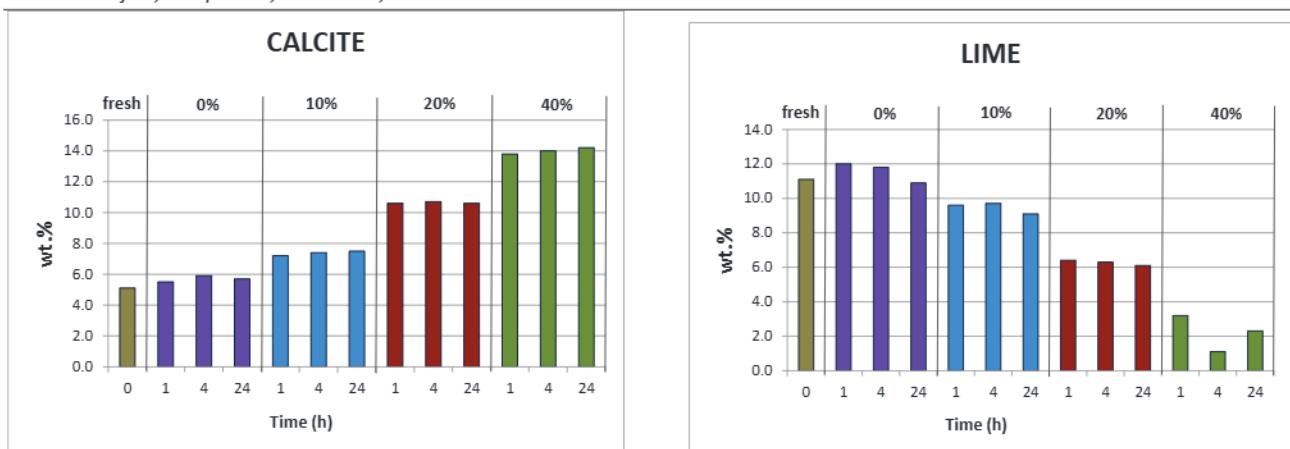


Figure 5. XRD results showing the progress of the carbonation process in co-combustion ash during the early stages (up to 24 hours), highlighting lime depletion and calcite formation.

5. Conclusions

This study evaluated the hydration behaviour and early carbonation potential of four combustion ashes—coal, co-combustion, paper sludge, and biomass—emphasizing their chemical, mineralogical, and microstructural variability. XRF and QXRD analyses showed that coal and co-combustion ashes are predominantly silico-aluminous, paper sludge ash is highly calcareous with elevated alkali content, and biomass ash is also calcareous. SEM/EDS observations confirmed differences in grain morphology as well as in the distribution and appearance of amorphous phases, both of which are critical for reactivity.

Hydration experiments demonstrated that paper sludge ash exhibited the most extensive formation of calcium aluminate hydrates, while coal and co-combustion ashes showed moderate hydration, and biomass ash formed only minor newly formed phases. Carbonation tests on co-combustion ash showed that lime transformed into calcite and other hydrated products, with higher moisture content and longer curing times (24 hours) enhancing slightly the carbonation process. Hydration and carbonation were observed to occur simultaneously, influencing both the kinetics and composition of hydration products.

These findings highlight the potential for valorising diverse combustion ashes in construction applications, supporting circular economy objectives. Understanding the coupled processes of hydration and carbonation is crucial for optimizing the performance and durability of ash-containing materials.

Future work will focus on identifying and clarifying the key factors controlling these processes, including the influence of ash amorphous phase composition, particle morphology, and environmental conditions, to enable more efficient and safe utilization of industrial by-products in construction materials.

6. References

Aboustait, M.; Kim, T.; Ley, M.T.; Davis, J.M. Physical and chemical characteristics of fly ash using automated scanning electron microscopy. *Constr. Build. Mater.*, 106, 1–10 (2016).

Ding, X.; Du, H.; Wu, E.; Yi, P.; Li, Y.; Luo, Y.; Liu, W. Investigating the hydration, mechanical properties, and pozzolanic activity of cement paste containing co-combustion fly ash. *Buildings*, 14, 1305 (2024).

European Commission. *The Raw Materials Initiative—Meeting Our Critical Needs for Growth and Jobs in Europe*; 699 final; COM: Brussels, Belgium, 2008.

European Commission. *Closing the Loop—An EU Action Plan for the Circular Economy*; 614 final; COM: Brussels, Belgium, 2015.

European Commission. *Critical Raw Materials Resilience: Charting a Path towards Greater Security and Sustainability*; 474 final; COM: Brussels, Belgium, 2020.

Gupta, S.; Kumar, A.; Singh, V.P.; Patel, P. Coal bottom ash and its applications in cement and concrete technologies: a review. *J. Mater. Circular Econ.*, 6(1), 23–45 (2024).

Hogg, D. *Incineration residues in the EU: quantities and fates*. Edited by E. Favoino, J. Vähk and A. Oliveira. Brussels: Zero Waste Europe (2022).

Li, C.; Zhang, Q.; Shi, C. Evolution of CO₂ uptake degree of ordinary Portland cement during accelerated aqueous mineralisation. *Minerals*, 7(4), 109 (2024).

Mohebbi, M.; Rajabipour, F.; Madadian, E. A framework for identifying the host phases in coal-derived fly ash. *Fuel*, 314, 122806 (2022).

NEPN. *Celoviti Nacionalni Energetski in Podnebni Načrt Republike Slovenije*; NEPN: Ljubljana, Slovenia (2020).

Oprčkal, P.; Mladenovič, A.; Zupančič, N.; Ščančar, J.; Milačič, R.; Zalar Serjun, V. Remediation of contaminated soil by red mud and paper ash. *J. Clean. Prod.*, 256, 120440 (2020).

Pihlajavaara, T.; Andersson, R.; Johansson, K. Enforced carbonation of cementitious materials: mechanisms and applications for industrial by-products. *Cem. Concr. Res.*, 176, 107028 (2023).

Rahman, A.; Torres, L.; Kim, S. Durability and environmental impact of wastewater sludge ash as a cement replacement in concrete: challenges and future directions. *Clean Technol. Recycl.*, 7(2), 145–162 (2025).

Shi, L.; Müller, A.; Koyanaka, S. Influence of amorphous content in recycled fly ash on binder hydration characteristics. *J. Mater. Cycles Waste Manag.*, 27, 112–124 (2025).

Singh, G.B.; Subramaniam, K.V. Quantitative XRD study of amorphous phase in alkali activated low-calcium siliceous fly ash. *Constr. Build. Mater.*, 124, 139–147 (2016).

SIST EN 16907-2. *Zemeljska Dela—2. Del: Klasifikacija Materialov*. iTeh Standards: Toronto, ON, Canada (2019).

Skevi, A.; Tsiamposi, A.; Papatzani, S. Biomass bottom ash as supplementary cementitious material: the effect of mechanochemical pre-treatment and mineral carbonation. *Sustainability*, 14(24), 16480 (2022).

Snellings, R.; Suraneni, P.; Skibsted, J. Future and emerging supplementary cementitious materials. *Cem. Concr. Res.*, 107199 (2023).

Wei, G.; Dong, B.; Fang, G.; Wang, Y. Understanding reactive amorphous phases of fly ash through the acidolysis. *Cem. Concr. Compos.*, 140, 105102 (2023).

Yao, Z.T.; Ji, X.S.; Sarker, P.K.; Tang, J.H.; Ge, L.Q.; Xia, M.S.; Xi, Y.Q. A comprehensive review on the applications of coal fly ash. *Earth-Sci. Rev.*, 141, 105–121 (2015).

Zalar Serjun, V. Recycling of different incineration ashes in the construction sector: perspectives from Slovenia. *Materials*, 16(12), 5065 (2024).

Zhao, P.; Liu, X.; De La Torre, A.G.; Lu, L.; Sobolev, K. Assessment of the quantitative accuracy of Rietveld/XRD analysis of crystalline and amorphous phases in fly ash. *Anal. Methods*, 9, 2415–2424 (2017).

Acknowledgment

Special thanks to dr. Mateja Štefancič for conducting the XRF analysis, Sabina Drmovšek for technical support and to dr. Ana Mladenovič for her contributions to the conceptualization of part of this work.

Funding

This research was funded by Slovenian Research and Innovation Agency (ARIS), grant numbers P2-0273, J1-4413 and J7-50228.

Author's contribution

All authors have contributed to: conceptualization, investigation, draft, and manuscript preparation.
All authors have read and agreed to the published version of the manuscript.