

Editorial

Editorial for Special Issue: Alkali Activated Materials: Advances, Innovations, Future Trends

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Alkali activated materials (AAMs), also named geopolymers or inorganic polymers, are materials that are produced when alkaline solutions react with precursors containing aluminosilicate phases [1–5]. The most commonly used alkaline solutions, include sodium or potassium hydroxides and/or silicates, while aluminosilicates may include suitable raw materials and by-products/wastes produced from various industrial processes. AAMs can be commercialized in various industrial sectors. When AAMs are produced with the use of industrial wastes, including for example metallurgical slags of various types [6,7], fly ashes [8,9], bauxite residues [10,11], construction and demolition wastes [12,13] or leaching residues [14], the benefits are twofold. They also include the valorization of these wastes for the production of value added products and the substantial reduction of the environmental footprint of the construction sector, due to the considerable savings of virgin raw materials [15–19].

This Special Issue of *Minerals* includes 14 papers highlighting the advances and future trends in alkali activation of wastes for the production of AAMs that can be used as sensors, adsorbents, catalysts, pH modifiers, as well as for the production of zeolite foams, low carbon binders, cemented paste backfill, alkali activated mortars and concrete. Furthermore, the elucidation of mechanisms involved during alkali activation, as well as the mineralogy, microstructure and properties of AAMs with the use of advanced techniques are discussed. All these papers aim to attract the interest of the readers and especially of young scientists and students at graduate and post-graduate levels in this very important scientific field.

Vlachakis et al. [20] in their review paper outlined the current state-of-the-art in strain, temperature and moisture sensors that can be developed with the use of AAMs, as main structural materials or as self-sensing coatings applied to existing infrastructure. One primary advantage of using AAMs for sensing is the elimination of the need for conductive fillers due to the migration of the alkali metal ions in their matrix. Sensor fabrication methods, electrical conductivity mechanisms, and comparisons with self-sensing ordinary Portland cement were outlined to highlight best practices and propose future research directions.

Medina et al. [21] investigated the adsorption efficiency of blast furnace slag (BFS) and fly ash (FA) based geopolymers, synthesized with the use of the hydrothermal method and cured at 60 °C, for the removal of Pb²⁺ ions from aqueous solutions. The alkali activator used was a mixture of NaOH and Na₂SiO₃ solutions at a mass ratio of 2, while the Si/Al molar ratio in the slurry was 3. The BFS-based geopolymers (GS) exhibited specific area ~25 m²/g, pore size ~8 nm and pore volume ~70 cm³/kg, while the FA-based geopolymers (GA) exhibited specific area ~35 m²/g, pore size 9 nm and porous volume ~125 cm³/kg. In addition, GS and GA exhibited cation exchange capacity (CEC) of ~240 and ~290 meq/100 g, respectively, at neutral pH and room temperature. Scanning electron microscopy (SEM) indicated that both geopolymers contained unreacted particles surrounded by amorphous and semi-amorphous phases, while Fourier transform infrared spectroscopy (FTIR) sug-



Citation: Komnitsas, K.A.; Bartzas, G. Editorial for Special Issue: Alkali Activated Materials: Advances, Innovations, Future Trends. *Minerals* **2021**, *11*, 75. <https://doi.org/10.3390/min11010075>

Received: 8 January 2021

Accepted: 8 January 2021

Published: 14 January 2021

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gested that Na and Ca can serve as exchangeable ions, thus increasing the adsorption efficiency of the produced geopolymers.

Kalinkin et al. [22] investigated the synthesis of geopolymers at ambient temperature, using NaOH solution as alkaline agent and blends of fly ash and calcite (0–10 wt.%), which were mechanically activated in a planetary mill. FTIR, isothermal conduction calorimetry, thermogravimetry coupled with mass spectrometry analysis of the evolved gas, and SEM/EDS were used to assess the effect of mechanical activation on the reactivity of the raw materials. The addition of calcite to fly ash improved the compressive strength of the geopolymers, especially at the early stage of curing. After an ageing period of 7 days, the geopolymers produced with the use of 90 wt.% fly ash + 10 wt.% calcite blend, acquired 8.0-, 3.5- and 2.9-fold higher strength compared to the geopolymers produced from pure fly ash after mechanical activation for 30 s, 180 s, and 400 s, respectively. The application of Mössbauer spectroscopy revealed that the iron present in the fly ash did not play a significant role in the geopolymerization process. The dominant reaction product was sodium containing aluminosilicate hydrogel (N-A-S-H gel). Calcite was transformed, to a small extent, to vaterite and $\text{Ca}(\text{OH})_2$ during geopolymerization.

Qiu et al. [23] investigated the potential of using alkali activated blast furnace slag (AAS) as low-carbon binder for the production of cemented paste backfill (CPB). With the use of orthogonal experimental design, the optimum parameters for the production of AAS binders and the flow ability of the fresh CPB slurry were determined. In addition, the toxicity of the binders, as indicated by the leaching of Pb and Cd ions, was assessed with the use of the Toxicity Characteristic Leaching Procedure (TCLP) test. Finally, a predictive model based on multivariate analysis for the determination of the compressive strength of CPB samples was developed.

Kou et al. [24] investigated the time-dependent rheological behavior of CPB containing alkali-activated slag (AAS) as binder, using the controlled shear strain method and various AAS-CPB samples with different binder content, silicate modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio), grain size of slag and curing temperature. The results showed that AAS-CPB samples with higher binder content exhibited a faster rate of increase for yield stress and plastic viscosity. They also exhibited better rheological behavior than CPB samples composed of ordinary Portland cement (OPC) and identical binder content. The increase in the particle size of slag had an adverse effect on the rheological behavior of AAS-CPB samples. Finally, the rheological behavior of both OPC- and AAS-CPB samples was substantially improved when higher curing temperature was used.

Bocullo et al. [25] investigated the effect of the addition of OPC and/or water glass for the production of fly ash (FA) alkali-activated concrete (AAC) and mortars. The results showed that FA concrete activated with the use of NaOH solution and water glass exhibited higher resistance to freeze and thaw, carbonation, alkali-silica reaction (ASR) and developed higher compressive strength and static elastic modulus compared with the FA concrete activated only with NaOH solution. The addition of OPC contributed to the development of denser microstructure for AAC. In the presence of water glass and OPC, the compressive strength of the specimens increased to ~53 MPa, which is more than two times higher than the reference sample (~21 MPa).

Gismera et al. [26] investigated the effect of the different particle size distribution of two precursors (slag and fly ash), and three types of aggregates (siliceous sand, limestone, and recycled concrete) on the rheology of AAM mortars and compared it with ordinary Portland Cement (OPC) reference mortars. Stress growth and flow curve tests were carried out to determine the plastic viscosity as well as the static and dynamic yield stress of the AAM and OPC mortars and was found that a reduction of the aggregate particle size resulted in an increase of the liquid demand to maintain their plastic consistency. The partial replacement of the siliceous aggregates with up to 20% recycled concrete did not affect the liquid uptake during the production of AAM or OPC mortars.

Vitola et al. [27] investigated the use of low-calcium porous AAMs as novel passive pH stabilizers in water media. The effect of the aluminosilicate source and heat treatment on

the main properties of the AAMs was assessed. The AAMs produced from fly ash exhibited higher bulk density (up to 750 kg/m^3), compared to those produced from metakaolin (up to 490 kg/m^3). The chemical composition of raw materials and especially the $\text{SiO}_2/\text{Na}_2\text{O}$ and $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ ratios affected the rate of zeolite formation, and thus, the structure of the AAMs. Heat treatment did not have any noticeable impact on the mineralogical composition and structure of the AAMs, but it affected the leaching of OH^- ions.

Tişler et al. [28] investigated in detail the effect of post-synthesis modification of alkali-activated natural zeolite foams on their chemical, mechanical and textural properties which can determine their use as catalysts or adsorbents. Modification was carried out with acid leaching, using mineral and organic acids, as well as with heat treatment up to 1000°C . Leaching resulted in the removal of elements from the structure, the purification of the micro- and mesopores in the zeolite matrix and the increase of the specific surface area to $350 \text{ m}^2/\text{g}$. Thermal treatment up to 600°C indicated that the basic clinoptilolite structure remained unaffected, while at higher temperature it was disintegrated and the foams were converted to inert macroporous ceramics, as demonstrated by x-ray diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and N_2 physisorption. On the same topic, Hrachovcová et al. [29] produced basic natural zeolite foams through alkali activation of natural zeolites using as activator KOH and Na_2SiO_3 solutions and as foaming agent hydrogen peroxide. These foams were compared with CaO, MgO and metakaolin modified zeolite foams. In this respect, the effect of the modification and the subsequent leaching on the textural, mechanical, and chemical properties was determined, with the use of Hg porosimetry, N_2 physisorption, NH_3 -TPD, XRF and XRD. From the data obtained, it was deduced that all modified zeolites exhibited increased strength and pore volume in the mesoporous region, while the surface area increased to values close to $290 \text{ m}^2/\text{g}$. As a result, they may be used as catalysts and adsorbents.

Ouyang et al. [30] investigated the effect of activator modulus ($\text{SiO}_2/\text{Na}_2\text{O}$) and slag addition on the properties of fresh and hardened alkali-activated fly ash/slag (AAFS) pastes. Four activator moduli ($\text{SiO}_2/\text{Na}_2\text{O}$) and five slag-to-binder ratios were studied. The setting time, the flowability, the heat evolution, the compressive strength, the microstructure and the reaction products of the AAFS pastes were determined. The results showed that the activator modulus and slag content had a combined effect on the setting behavior and workability of the AAFS mixtures. The dissolution of elements from slag was more pronounced when NaOH was used as activator. The use of Na_2SiO_3 significantly refined the pores in AAFS mixtures by incorporating soluble Si, while further increase of the modulus from the optimum value of 1.5 to 2.0 had an adverse effect, resulting in lower heat release, coarser pore structure and reduced compressive strength.

Kioupis et al. [31] investigated the synthesis of geopolymeric binders from construction and demolition wastes (CDW). Ceramic waste was the only aluminosilicate precursor used, while glass waste after appropriate processing was used for the preparation of the activating solution. A fractional experimental design was used and the optimum synthesis parameters were defined, based on compressive strength values. The final products were characterized by means of XRD, FTIR and SEM. The CDW-based geopolymers produced acquired compressive strength in the range of 10–44 MPa. The developed products contained 80–90 wt.% CDWs, indicating the noticeable valorization potential of this waste stream which is produced in large quantities worldwide.

Petrakis et al. [32] studied the grinding process of a Polish ferronickel slag and evaluated the particle size distributions (PSDs) of the products obtained after the use of different grinding times. It was found that grinding exhibits non-first-order behavior and the reduction rate of each size is time dependent. Among the different models tested to simulate the PSD, Rosin–Rammler (RR) was found to be the most suitable. Furthermore, selected grinding products were alkali activated in order to investigate the effect of particle size on the compressive strength of the produced AAMs. Among the parameters studied, particle size of the raw slag and curing temperature had the most noticeable impact on compressive strength, the maximum value of which reached ~ 60 MPa.

Finally, Komnitsas et al. [33] explored the valorization potential of marble waste with the addition of metakaolin, via alkali activation. The activating solution used consisted of NaOH and sodium silicate solutions. The effects of marble waste to metakaolin ratio, particle size of raw materials, curing temperature, and Na₂O/SiO₂ and H₂O/Na₂O molar ratios present in the activating solution on the main properties and the morphology of the produced AAMs were evaluated. The durability and structural integrity of the AAMs after firing them at temperatures between 200 and 600 °C, immersion in deionized water and 1 mol/L NaCl solution for different time periods and subjection to freeze–thaw cycles were also investigated. The highest compressive strength (~36 MPa) was acquired by AAMs prepared using precursors with marble waste to metakaolin mass ratio of 0.3 after curing at 40 °C.

Author Contributions: K.A.K. and G.B. wrote this editorial. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The availability of data has been defined in each paper published in this special issue.

Acknowledgments: The guest editors would like to sincerely thank all authors, reviewers and the editorial staff of *Minerals* for their efforts and devotion to successfully complete this Special Issue.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Davidovits, J. Geopolymers—Inorganic polymeric new materials. *J. Therm. Anal. Calorim.* **1991**, *37*, 1633–1656. [[CrossRef](#)]
2. Komnitsas, K.; Zaharaki, D. Geopolymerisation: A review and prospects for the minerals industry. *Miner. Eng.* **2007**, *20*, 1261–1277. [[CrossRef](#)]
3. Duxson, P.; Fernández-Jiménez, A.; Provis, J.L.; Lukey, G.C.; Palomo, A.; Van Deventer, J.S.J. Geopolymer technology: The current state of the art. *J. Mater. Sci.* **2007**, *42*, 2917–2933. [[CrossRef](#)]
4. Provis, J.L.; Bernal, S.A. Geopolymers and related alkali-activated materials. *Annu. Rev. Mater. Res.* **2014**, *44*, 229–327. [[CrossRef](#)]
5. Peys, A.; Douvalis, A.P.; Siakati, C.; Rahier, H.; Blanpain, B.; Pontikes, Y. The influence of air and temperature on the reaction mechanism and molecular structure of Fe-silicate inorganic polymers. *J. Non-Cryst. Solids* **2019**, *526*, 119675. [[CrossRef](#)]
6. Komnitsas, K.; Bartzas, G.; Karmali, V.; Petrakis, E.; Kurylak, W.; Pietek, G.; Kanasiewics, J. Assessment of alkali activation potential of a Polish ferronickel slag. *Sustainability* **2019**, *11*, 1863. [[CrossRef](#)]
7. Sun, J.; Zhang, Z.; Zhuang, S.; He, W. Hydration properties and microstructure characteristics of alkali-activated steel slag. *Constr. Build. Mater.* **2020**, *241*, 118141. [[CrossRef](#)]
8. Mondal, S.K.; Welz, A.; Rownaghi, A.; Wang, B.; Ma, H.; Rezaei, F.; Kumar, A.; Okoronkwo, M.U. Investigating the microstructure of high-calcium fly ash-based alkali-activated material for aqueous Zn sorption. *Environ. Res.* **2020**, 110484. [[CrossRef](#)]
9. Rivera, J.F.; de Gutiérrez, R.M.; Ramirez-Benavides, S.; Orobio, A. Compressed and stabilized soil blocks with fly ash-based alkali-activated cements. *Constr. Build. Mater.* **2020**, *264*, 120285. [[CrossRef](#)]
10. Hertel, T.; Pontikes, Y. Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud)—Putting things in perspective. *J. Clean. Prod.* **2020**, *258*, 120610. [[CrossRef](#)]
11. Croymans, T.; Schroeyers, W.; Krivenko, P.; Kovalchuk, O.; Pasko, A.; Hult, M.; Marissens, G.; Lutter, G.; Schreurs, S. Radiological characterization and evaluation of high volume bauxite residue alkali activated concretes. *J. Environ. Radioact.* **2017**, *168*, 21–29. [[CrossRef](#)] [[PubMed](#)]
12. Komnitsas, K.; Zaharaki, D.; Vlachou, A.; Bartzas, G.; Galetakis, M. Effect of synthesis parameters on the quality of construction and demolition wastes (CDW) geopolymers. *Adv. Powder Technol.* **2015**, *26*, 368–376. [[CrossRef](#)]
13. Bassani, M.; Tefa, L.; Russo, A.; Palmero, P. Alkali-activation of recycled construction and demolition waste aggregate with no added binder. *Constr. Build. Mater.* **2019**, *205*, 398–413. [[CrossRef](#)]
14. Komnitsas, K.; Petrakis, E.; Bartzas, G.; Karmali, V. Column leaching of low-grade saprolitic laterites and valorization of leaching residues. *Sci. Total Environ.* **2019**, *665*, 347–357. [[CrossRef](#)]
15. Komnitsas, K. Potential of geopolymer technology towards green buildings and sustainable cities. *Procedia Eng.* **2011**, *21*, 1023–1032. [[CrossRef](#)]

16. Shekhovtsova, J.; Zhernovsky, I.; Kovtun, M.; Kozhukhova, N.; Zhernovskaya, I.; Kearsley, E. Estimation of fly ash reactivity for use in alkali-activated cements—A step towards sustainable building material and waste utilization. *J. Clean. Prod.* **2018**, *178*, 22–33. [[CrossRef](#)]
17. Abdulkareem, M.; Havukainen, J.; Nuortila-Jokinen, J.; Horttanainen, M. Environmental and economic perspective of waste-derived activators on alkali-activated mortars. *J. Clean. Prod.* **2021**, 124651. [[CrossRef](#)]
18. Robayo-Salazar, R.; Mejía-Arcila, J.; Mejía de Gutiérrez, R.; Martínez, E. Life cycle assessment (LCA) of an alkali-activated binary concrete based on natural volcanic pozzolan: A comparative analysis to OPC concrete. *Constr. Build. Mater.* **2018**, *176*, 103–111. [[CrossRef](#)]
19. Huseien, G.F.; Shah, K.W. Durability and life cycle evaluation of self-compacting concrete containing fly ash as GBFS replacement with alkali activation. *Constr. Build. Mater.* **2020**, *235*, 117458. [[CrossRef](#)]
20. Vlachakis, C.; Perry, M.; Biondi, L. Self-sensing alkali-activated materials: A review. *Minerals* **2020**, *10*, 885. [[CrossRef](#)]
21. Medina, T.J.; Arredondo, S.P.; Corral, R.; Jacobo, A.; Zárraga, R.A.; Rosas, C.A.; Cabrera, F.G.; Bernal, J.M. Microstructure and Pb²⁺ adsorption properties of blast furnace slag and fly ash based geopolymers. *Minerals* **2020**, *10*, 808. [[CrossRef](#)]
22. Kalinkin, A.M.; Gurevich, B.I.; Myshenkov, M.S.; Chislov, M.V.; Kalinkina, E.V.; Zvereva, I.A.; Cherkezova-Zheleva, Z.; Paneva, D.; Petkova, V. Synthesis of fly ash-based geopolymers: Effect of calcite addition and mechanical activation. *Minerals* **2020**, *10*, 827. [[CrossRef](#)]
23. Qiu, J.; Zhao, Y.; Long, H.; Guo, Z.; Xing, J.; Sun, X. Low-carbon binder for cemented paste backfill: Flowability, strength and leaching characteristics. *Minerals* **2019**, *9*, 707. [[CrossRef](#)]
24. Kou, Y.; Jiang, H.; Ren, L.; Yilmaz, E.; Li, Y. Rheological properties of cemented paste backfill with alkali-activated slag. *Minerals* **2020**, *10*, 288. [[CrossRef](#)]
25. Bocullo, V.; Vaičiukynienė, D.; Gečys, R.; Daukšys, M. Effect of ordinary Portland cement and water glass on the properties of alkali activated fly ash concrete. *Minerals* **2020**, *10*, 40. [[CrossRef](#)]
26. Gismara, S.; Alonso, M.D.M.; Palacios, M.; Puertas, F. Rheology of alkali-activated mortars: Influence of particle size and nature of aggregates. *Minerals* **2020**, *10*, 726. [[CrossRef](#)]
27. Vitola, L.; Bajare, D.; Palomo, A.; Fernandez-Jimenez, A. Low-calcium, porous, alkali-activated materials as novel pH stabilizers for water media. *Minerals* **2020**, *10*, 935. [[CrossRef](#)]
28. Tišler, Z.; Hrachovcová, K.; Svobodová, E.; Šafář, J.; Pelíšková, L. Acid and thermal treatment of alkali-activated zeolite foams. *Minerals* **2019**, *9*, 719. [[CrossRef](#)]
29. Hrachovcová, K.; Tišler, Z.; Svobodová, E.; Šafář, J. Modified alkali activated zeolite foams with improved textural and mechanical properties. *Minerals* **2020**, *10*, 483. [[CrossRef](#)]
30. Ouyang, X.; Ma, Y.; Liu, Z.; Liang, J.; Ye, G. Effect of the Sodium Silicate Modulus and Slag Content on Fresh and Hardened Properties of Alkali-Activated Fly Ash/Slag. *Minerals* **2020**, *10*, 15. [[CrossRef](#)]
31. Kioupis, D.; Skaropoulou, A.; Tsivilis, S.; Kakali, K. Valorization of brick and glass cdws for the development of geopolymers containing more than 80% of wastes. *Minerals* **2020**, *10*, 672. [[CrossRef](#)]
32. Petrakis, E.; Karmali, V.; Bartzas, G.; Komnitsas, K. Grinding kinetics of slag and effect of final particle size on the compressive strength of alkali activated materials. *Minerals* **2019**, *9*, 714. [[CrossRef](#)]
33. Komnitsas, K.; Soultana, A.; Bartzas, G. Marble waste valorization through alkali activation. *Minerals* **2021**, *11*, 46. [[CrossRef](#)]