Geopolymers

Subjects: Engineering, Environmental
Contributor: Mohd Mustafa Al Bakri Abdullah , Rafiza Abd Razak , Liyana Jamaludin , Petrica Vizureanu , Ana Bras , Thanongsak Imjai , Andrei Victor Sandu , Shayfull Zamree Abd Rahim , Heah Cheng Yong

Geopolymers represent novel material types at the interface of glass, ceramics, and materials based on traditional inorganic bonds. Geopolymers utilize waste materials as source material and activate the materials with alkaline activators to act as binders. Metakaolin is categorised as an aluminosilicate material because it contains variable amounts of alumina and silica. Geopolymers offer benefits due to their ease of synthesis and low emissions of greenhouse gases such as CO_2, SO_2, and NO_x.

photocatalytic geopolymer coating

1. Geopolymer Aluminosilicate Materials

Geopolymers result from the interactions of inorganic elements like coal fly ash and incinerator ash, slags such granulated blast (steel) or furnace (iron) slag, and clays like metakaolin or calcined clay [1][2] with an alkaline activator. Geopolymers focus on utilizing waste products to create value. Other industrial wastes included glass, melt-quenched aluminosilicates, natural minerals such as kaolinite and natural zeolite, volcanic ash, and mine tailing, waste ceramics, and catalyst residues, as well as mixtures of these materials [3][4]. Fly ash and metakaolin are the most frequent aluminosilicates or raw materials employed by researchers to construct traditional geopolymer adsorbents. Geopolymers incorporate waste materials as source materials and an alkaline activator to serve as a binder. Commonly, the alkaline liquid utilised in geopolymerization is a mixture of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) [5][6]. Geopolymerization is a heterogeneous chemical reaction involving solid aluminosilicate oxides and alkali metal silicate solutions under very alkaline conditions and low temperatures that produces amorphous to semicrystalline polymeric structures composed of Si-O-Al and Si-O-Si bonds [7][8]. Geopolymerization entails a very rapid chemical reaction under alkaline circumstances with Si and Al minerals, resulting in a three-dimensional polymeric chain and ring structure composed of Si-O-Al-O bond [9].

Kaolin has high concentrations of SiO_2 and AlO_3 depending on the place of extraction. Kaolin is then extracted and subjected to the calcination process, which seeks to produce a material with pozzolanic features and high reactivity. Metakaolin ($Al_2Si_2O_7$) is made from kaolin clay. An amorphous kaolinite produced by treatment at 500 to 800 °C was used to convert kaolin to metakaolin [10][11]. The Al (VI) in kaolinite is converted into Al (IV) and Al (V) in this process to generate amorphous aluminium silicate. Spinel, mullite, and other crystals are formed when a high temperature is maintained constantly throughout the calcination process. Al (IV) and Al (V) will be changed into Al (VI) through this procedure [12]. In strong alkali solutions, metakaolin dissolves and releases Al and Si rapidly, producing geopolymer, zeolite, and other compounds depending on the reaction environment [13]. Metakaolin has substantially greater activity than kaolin in the same environment, which expands the application range of metakaolin, especially as geopolymer material.

Fly ash is a solid fine residue formed of particles expelled from the boilers of coal-fired power plants with flue gases [9][14][15]. Fly ash is used in the development of geopolymers because of its naturally high concentrations of SiO_2 and Al_2O_3; low SiO_2 and Al_2O_3 content is insufficient for alkali activation [16].

Slag is a by-product of the production of wrought iron and steel. As by-products of metallurgical operations or incineration processes, many slags are formed. In slag-blended systems, the geopolymerization reaction rate rises with increasing slag and activator concentrations [17]. **Table 1** summarises the most recent published research on aluminosilicate materials. The table includes the aluminosilicate materials and the research findings. This summary shows that researchers are focusing more on using geopolymer aluminosilicate materials for concrete and cement applications and less on using the geopolymer materials for coating applications.

Table 1. Aluminosilicate materials used in the recent research on geopolymers.

Author	Aluminosilicate Material	Finding
Yusuf G. Adewuyi [9]	Class F Fly Ash	Elimination of trace noxious heavy metals in aqueous environment. The geopolymer adsorbent as a substance is recyclable since it can be synthesized by leveraging abundant waste materials.
Rafik Abbas et al. [18]	Kaolin	Used to produce geopolymer concrete as it does not require energy for pretreatment and contains high alumina silicate.
Abdulrahman et al. [19]	Metakaolin	Metakaolin geopolymer with different mix design for producing geopolymer concrete.
Ionescu et al. [20]	Slag	Steel slag or blast furnace slag in the production of geopolymer for construction building materials

2. Factor Affecting Geopolymer Paste

Geopolymerization reaction required numerous parameters to consider. One of the most significant variables in this regard is determining the physical properties and chemical composition of the raw material, since this influences the activator’s alkaline degree.

Though since raw materials differ from batch to batch (minerals or waste materials, for example), it is critical to thoroughly analyse the samples before adjusting the composition and amount of the activating solution based on solid to liquid ratio, and percentage of photocatalyst precursor. The solid-to-liquid (S/L) ratio influences the characteristics of geopolymer paste. Jaya et al. [21] exposed the influence of numerous S/L ratio ranging from 0.6 to 0.8. It was found that 0.76 is the optimal ratio for S/L ratios. Compared to the others, the surface of geopolymer with an optimum S/L ratio was more homogenous, dense, and porous due to high strength. The high compressive strength proved by the phase analysis revealed no traces of zeolite crystal peaks. Guzman-Aponte et al. [22] on the other hand, employed a 0.8 ratio to achieve good workability in their investigation. Previous research from Guzman-Aponte et al. [23] discussed liquid/solid ratio (L/S) was also varied in three levels, 0.35 (dry consistency), 0.40 (mean consistency), and 0.45 (fluid consistency). The results indicate that increased liquid content can promote the speed of dissolution of the Al and Si species of the precursor, but it obstructs the processes of polycondensation. Albidah et al. [19] study the solid to liquid ratio ranging from 0.3 to 0.8 shows hen alkaline solids to MK ratio increased from 0.37 to 0.41, the compressive strength dropped from 58.5 to 39.7 MPa. The strength reduction can be attributed to the excess amount of silica content as the SiO_2/Al_2O_3 molar ratio was increased from 2.69 to 2.75, which can contribute to the impedance of geopolymerization process. Yaacob et al. [24] used a S/L ratio of 0.33 to produce a geopolymer coating with maximum adhesion strength of 3.8 MPa.

In addition to the solid-to-liquid ratio, the percentage of photocatalyst precursor also plays an important role in enhancing the photocatalytic performance of geopolymer pastes suitable for coating. Wang et al. [25] discovered that 5 wt.% TiO_2 resulted in the most efficient photocatalytic based on methylene blue colour alteration. Setting time and leaching studies demonstrate that Zn has a much stronger retarding impact on reaction kinetics in Na-activated geopolymers compared with K-activated geopolymers. However, Na-activated geopolymers have a better fixing ability to Zn. In the Zn-substituted geopolymer system, Al_2O_3/M_2O ratio was 0.8 and ZnO/M_2O ratio was 0.2 respectively. According to Guzmán-Aponte et al. [23] the percentage of TiO_2 addition as a function of cement was revised at three levels; 0 wt.%, 5 wt.% and 10 wt.%. This amount of TiO_2 effect the performance of photocatalytic efficiency by improving the carbonation process and band gap energy. The results show that a percentage of TiO_2 up to 10% has no influence on the mechanical characteristics of geopolymer and the production of the K-A-S-H gel. According to Zidi et al. [10] the optimal quantity of nano-ZnO to enhance the mechanical and structural of metakaolin geopolymer was 0.5 wt.%. The incorporation of nano-ZnO enhanced pulsed velocity and boosted compressive strength from 30 to 38 MPa. The optimum percentage of ZnO was found to be 0.5 wt.% according to research from Wang et al. [25], ZnO responded fully and formed amorphous products after 7 days of curing. The crystallinity phases of a metakaolin geopolymer paste are unaffected by the addition of ZnO nanoparticles as a photocatalyst. Aside from that, Zailan et al. [26] prepared the TiO_2 geopolymer paste by varying the percentage of nano-TiO_2, which are 5.0 wt.%, 10.0 wt.% and 15.0 wt.%. The study discovered the methylene blue discoloration after exposure to sunlight up to 150 min with great photocatalytic effect. Strini et al. [27] added 3% of TiO_2 by weight paste into the fly ash and metakaolin geopolymer. The findings demonstrated that geopolymer binders can be effective catalyst support matrices for the coating applications. Based on the studies from other researchers, less research regarding addition of photocatalyst precursor into the geopolymer paste for coating characterization and this gap can be fulfilled.

References

1. 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.

2. Blissett, R.S.; Rowson, N.A. A Review of the Multi-Component Utilisation of Coal Fly Ash. Fuel 2012, 97, 1–23.
3. Falah, M.; Mackenzie, K.J.D. Photocatalytic Nanocomposite Materials Based on Inorganic Polymers (Geopolymers): A Review. Catalysts 2020, 10, 1158.
4. Siyal, A.A.; Shamsuddin, M.R.; Khan, M.I.; Rabat, N.E.; Zulfiqar, M.; Man, Z.; Siame, J.; Azizli, K.A. A Review on Geopolymers as Emerging Materials for the Adsorption of Heavy Metals and Dyes. J. Environ. Manag. 2018, 224, 327–339.
5. Davidovits, J. Geopolymers. J. Therm. Anal. 1991, 37, 1633–1656.
6. Saloma; Hanafiah; Elysandi, D.O.; Meykan, D.G. Effect of Na2SiO3/NaOH on Mechanical Properties and Microstructure of Geopolymer Mortar Using Fly Ash and Rice Husk Ash as Precursor. AIP Conf. Proc. 2017, 1903, 050013.
7. Al Bakri, A.M.; Kamarudin, H.; Bnhussain, M.; Nizar, I.K.; Mastura, W. Mechanism and Chemical Reaction of Fly Ash Geopolymer Cement—A Review. J. Asian Sci. Res. 2011, 1, 247–253.
8. Castillo, H.; Collado, H.; Droguett, T.; Vesely, M.; Garrido, P.; Palma, S. State of the Art of Geopolymers: A Review. E-Polymer 2022, 22, 108–124.
9. Adewuyi, Y.G. Recent Advances in Fly-Ash-Based Geopolymers: Potential on the Utilization for Sustainable Environmental Remediation. ACS Omega 2021, 6, 15532–15542.
10. Zidi, Z.; Ltifi, M.; ben Ayadi, Z.; Mir, L.E.L.; Nóvoa, X.R. Effect of Nano-ZnO on Mechanical and Thermal Properties of Geopolymer. J. Asian Ceram. Soc. 2020, 8, 1–9.
11. Cao, R.; Fang, Z.; Jin, M.; Shang, Y. Study on the Activity of Metakaolin Produced by Traditional Rotary Kiln in China. Minerals 2022, 12, 365.
12. Rocha, J.; Klinowski, J. Physics and Chemistry of Minerals, 295i and 27A1 Magic-Angle-Spinning NMR Studies of the Transformation of Kaolinite; University of Cambridge: Cambridge, UK, 1990; Volume 17.
13. De Rossi, A.; Simão, L.; Ribeiro, M.J.; Novais, R.M.; Labrincha, J.A.; Hotza, D.; Moreira, R.F.P.M. In-Situ Synthesis of Zeolites by Geopolymerization of Biomass Fly Ash and Metakaolin. Mater. Lett. 2019, 236, 644–648.
14. Zhuang, X.Y.; Chen, L.; Komarneni, S.; Zhou, C.H.; Tong, D.S.; Yang, H.M.; Yu, W.H.; Wang, H. Fly Ash-Based Geopolymer: Clean Production, Properties and Applications. J. Clean. Prod. 2016, 125, 253–267.
15. Kalombe, R.M.; Ojumu, V.T.; Eze, C.P.; Nyale, S.M.; Kevern, J.; Petrik, L.F. Fly Ash-Based Geopolymer Building Materials for Green and Sustainable Development. Materials 2020, 13, 5699.

16. Prochon, P.; Zhao, Z.; Courard, L.; Piotrowski, T.; Michel, F.; Garbacz, A. Influence of Activators on Mechanical Properties of Modified Fly Ash Based Geopolymer Mortars. Materials 2020, 13, 1033.
17. Humad, A.M.; Kothari, A.; Provis, J.L.; Cwirzen, A. The Effect of Blast Furnace Slag/Fly Ash Ratio on Setting, Strength, and Shrinkage of Alkali-Activated Pastes and Concretes. Front. Mater. 2019, 6, 9.
18. Abbas, R.; Khereby, M.A.; Ghorab, H.Y.; Elkhoshkhany, N. Preparation of Geopolymer Concrete Using Egyptian Kaolin Clay and the Study of Its Environmental Effects and Economic Cost. Clean Technol. Environ. Policy 2020, 22, 669–687.
19. Albidah, A.; Alghannam, M.; Abbas, H.; Almusallam, T.; Al-Salloum, Y. Characteristics of Metakaolin-Based Geopolymer Concrete for Different Mix Design Parameters. J. Mater. Res. Technol. 2021, 10, 84–98.
20. Ionescu, B.A.; Lăzărescu, A.-V.; Hegyi, A. The Possibility of Using Slag for the Production of Geopolymer Materials and Its Influence on Mechanical Performances—A Review. Proceedings 2020, 63, 30.
21. Jaya, N.A.; Abdullah, M.M.A.B.; Li, L.-Y.; Sandu, A.V.; Hussin, K.; Ming, L.Y. Durability of Metakaolin Geopolymers with Various Sodium Silicate/Sodium Hydroxide Ratios against Seawater Exposure. AIP Conf. Proc. 2017, 1887, 020063.
22. Guzmán-Carrillo, H.R.; Manzano-Ramírez, A.; Garcia Lodeiro, I.; Fernández-Jiménez, A. ZnO Nanoparticles for Photocatalytic Application in Alkali-Activated Materials. Molecules 2020, 25, 5519.
23. Guzmán-Aponte, L.A.; de Gutiérrez, R.M.; Maury-Ramírez, A. Metakaolin-Based Geopolymer with Added TiO2 Particles: Physicomechanical Characteristics. Coatings 2017, 7, 233.
24. Yaakob, S.M.; Rabat, N.E.; Sufian, S. Effects of Na: Al and Water: Solid Ratios on the Mechanical Properties of Fly Ash Based Geopolymer. IOP Conf. Ser. Mater. Sci. Eng. 2018, 458, 012011.
25. Wang, L.; Geddes, D.A.; Walkley, B.; Provis, J.L.; Mechtcherine, V.; Tsang, D.C.W. The Role of Zinc in Metakaolin-Based Geopolymers. Cem. Concr. Res. 2020, 136, 106194.
26. Zailan, S.N.; Mahmed, N.; Abdullah, M.M.A.B. Photocatalytic Behaviour of TiO2-Geopolymer Paste under Sunlight. IOP Conf. Ser. Mater. Sci. Eng. 2020, 957, 012006.
27. Strini, A.; Roviello, G.; Ricciotti, L.; Ferone, C.; Messina, F.; Schiavi, L.; Corsaro, D.; Cioffi, R. TiO2-Based Photocatalytic Geopolymers for Nitric Oxide Degradation. Materials 2016, 9, 513.