Metal oxide (V_2O_5) incorporated fly ash based geopolymer for better sustainable engineering composites

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Abstract

During the coal-burning process, fly ash is produced as a by-product and disposal of this vast waste material is becoming challenge in the current environmental scenario. In the present work, metal oxide V_2O_5 with different weights (3% and 5%) of fly ash was utilized in presence of alkaline activators to lower the mullitization temperature below to 1000 ºC for the development of new concrete approaches. The building composites were made by using sintered fly ash and alkaline activators at ambient temperature. The micro structural analysis (XRD, FESEM, EDX) of the composites reveals the formation of needle like nano sized mullite at 1000 ºC. The durability and mechanical strengths tests including, compressive strength, flexural strength, split tensile strength, chloride ion permeability, water absorption and ultrasonic pulse velocity were conducted on the composites specimens. The experimental tests confirm the better strength and enhanced durability properties of the newly formed building composites. The study suggested a new methodology to utilize the waste material fly ash with vanadium oxide as an alternative cementitious material for advanced durable building composites. Copyright © 2019 VBRI Press.

Keywords: Fly ash, metal oxide, mullite, composite, strength, durability.

Introduction

The one tonne of cement production resulting of CO_2 emissions about 0.83 tonnes into the atmosphere. Also largest volume of concrete produces globally of 10 km^3/ year, and this amount further increase resulting from gigantic urban infrastructure development [**1**]. Therefore, various alternative materials have been used in cementitious materials by different researchers for achievement of higher mechanical strengths of the infrastructures and reduction of the massive amount of CO_2 release. On the other hand, the increasing accumulation of fly ash from enormous application of thermal power plants possesses an additional concern to the environment. Fly ash is commonly disposed of in landfills fill-up, however the proper consumption of fly ash is still very low percentage [**2**]. In this perspective, utilization of waste material i.e, fly ash in a construction technology is new hope as an alternative cementitious material which has potential to decrease the CO_2 footprint. Different conventional techniques have been made for using the waste material in different sectors to reduce environmental pollution [**3, 4**].

Recently, geopolymer comprises of fly ash, gained popularity due to their eco-friendly nature in terms of high early-age strength, low permeability, resistance to acid attack, good resistance to freeze–thaw cycles and fire resistance [**5-7**]. The geopolymers are produced by the dissolution of aluminosilicate species in an alkaline environment to form an amorphous 3D aluminosilicate gel structures by polycondensation reaction; therefore, it has possess cement like characteristics [**8**]. Recently Maiti *et al.* [**9**] prepared a building composite which has tendency to significantly remove the most heavy metal ions and dye degradation contained within the geopolymeric structure.

The alkali activation of fly ash usually requires high sintering temperature to form an effective composite material like the mullite, mullite ceramics and mullite whiskers from the fly ash [**10-12**]. Research has been focused on exploring the new methods and technologies with the purpose of decreasing the sintering temperature and densifying the end product of mullite. Our main objective is to reduce the high sintering temperature by incorporation of V_2O_5 metal oxide at lower concentration to prepare a high strength geopolymer under ambient temperature. The mechanical along-with durability properties of this material are thoroughly investigated and the micro structural analysis is performed by XRD, FESEM and EDX techniques.

Experimental details

Materials

Low Calcium Class F fly-ash, sand, sodium hydroxide (NaOH), Liquid sodium silicate (Na_2SiO_3) were used for the synthesis of geopolymer. For this study, vanadium pentoxide (V_2O_5) as the main metal oxide was purchased from sigma. Pvt. Ltd, USA and employed.

Material synthesis

Firstly, fly ash was mixed with the vanadium pentoxide (V_2O_5) in different weight ratios (3% and 5%). After that, the Fly ash – V_2O_5 mixtures were sintered at 1000 ºC for 150 min and left for few hours to cool down at normal temperature. The sintered flyash and 3% V_2O_5 mixture was named as FV3 and the sintered flyash and 5% V_2O_5 mixture was marked as FV5. The geopolymer was made by these two types of mixtures with alkali activators as per **Table 1**. Also, for the reference the geopolymer without V_2O_5 named as GM is also given in Table1. Alkali activator was prepared by 12M NaOH and Na_2SiO_3 solution with the 1:2 mixing ratio. The Fly ash and sand ratio was maintained at 1:3 and flyash to alkali activator ratio was fixed at 1:0.5.

Table 1. Sample preparation.

Sample	Mix proportion
GM	FA+ Alkali Activator + sand
GM3	FV3+ Alkali Activator + sand
GM5	FV5+ Alkali Activator + sand

Application for concrete study

The synthesized geopolymer was given specific dimension for various tests. For the compressive strength measurements, the cube specimen of dimension 50mm × 50 mm was made and test was conducted as per ASTM C109/C109M [**13**]. The flexural strength test was performed on the mortar samples of 160mm × 40mm × 40mm dimension beam samples. The cylindrical samples of dimension 100mm × 50mm was prepared for the split tensile strength measurement.

Durability properties in terms of rapid chloride permeability test (RCPT) and water absorption test as per ASTM C1202 and Neville's method respectively were conducted [**14, 15**]. The ultrasonic pulse velocity (UPV) of these samples was measured before applying the breaking load as per ASTM C597-02 [**16**].

All the geopolymeric mortar samples were prepared and air cured at ambient temperature for 28 days. For each category of geopolymer mortars, 5 samples were prepared and their average values were calculated.

Microstructural study

The broken mortar samples were collected after compressive strength measurement and crushed into powder samples of <5µm size for micro structural studies. The XRD test was performed by using X-ray diffractometer (X'Pert3 powder machine) with Cu Kα radiation and scan speed was fixed 0.5 s/step in the scanning range (2θ) from 10 to 80 degree at 40 kV and 30 mA. The morphological inspection was carried out by using Field Emission Scanning Electron Microscope (FESEM, SU8010) and elemental analysis was done by Energy dispersive X-Ray spectroscopy (EDX) equipped with FESEM machine.

Results and discussion

The class F fly ash was meticulously mixed with vanadium pentoxide (V_2O_5) and sintered at 1000 ºC.

For samples FV3 and FV5 mullite whiskers and needle like shaped mullite were formed. It is worthy to note here that although fly ash sintered at a same temperature i.e. 1000 ºC, the formation of mullite contents increase with the dosage of V_2O_5. In other words, the highest amount of mullite forms in the case of 5% V_2O_5. Similar results were found in study [**17**] . This shows V_2O_5 helps the formation of the liquid phase and encourages the sintering process.

In order to study the durability properties of the geopolymers specimens the ultrasonic pulse velocity through all the specimens were measured before conducting the compressive strength test. The results are shown in the **Fig. 2** and it can be observed that the higher pentoxide V_2O_5 incorporated in the fly ash geopolymers gave the higher values of ultrasonic pulse velocity (**Fig. 1**).

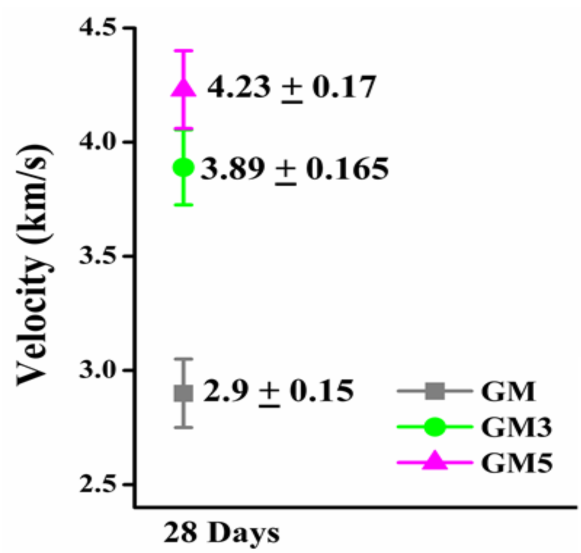

Fig. 1. Ultrasonic pulse velocity.

For comparison the UPV value of GM is taken as reference. The UPV values of GM3 and GM5 mortars samples increased considerably with respect to GM mortar sample. The higher values of UPV in GM5 mortar sample shows the better quality of cementitious composites possibly due to the denser and less porous structure. The key reason is that the nano size whisker formation in the end product reduces the pore size of the sample and hence decreases the porosity. As in case of porous material some amount of ultrasonic wave energy is vanished during impact which is possibly the reason of the lower values found in GM and GM3 mortar samples. The lower porosity and higher density of GM5 specimen make it durable mortar.

The results of water absorption test are presented in **Fig. 2**. It is noted that the GM and GM3 mortar sample have greater water absorption, while GM5 mortar sample has much lower value. The mass percentage increment of GM5 sample is about 4.22% and 4.67% for 30 minutes and 24 hours respectively. The lower water absorption confirms the less porous and compact structure of the GM5 sample.

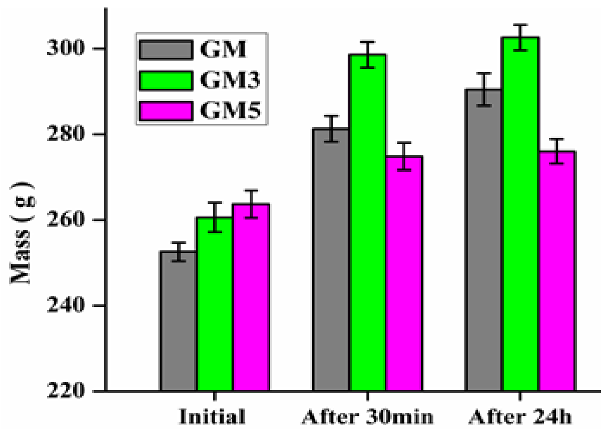

Fig. 2. Water Absorption test.

The RCPT is a common way to evaluate the permeability of different types of cementitious materials. **Fig. 3** depicted the results of RCPT test. It is evident from the figure that the smallest amount of chloride ion penetrate through the GM5 sample and the charge passed is about 419 Coulomb for 28 days of curing, which further supports the less porous structure of the sample [**18**].

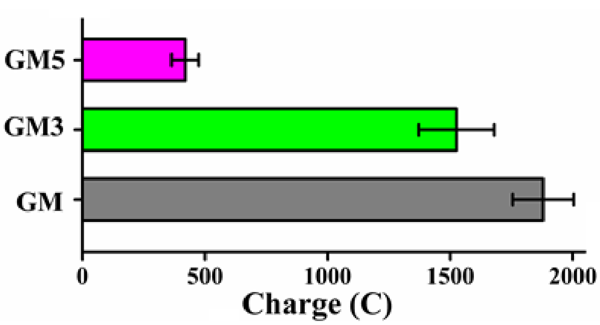

Fig. 3. Rapid Chloride ion permeability test (RCPT).

Fig. 4 shows the average compressive strength of GM, GM3 and GM5 samples. It is clearly seen that the GM sample has lower compressive strength value 25.24 MPa. When pentoxide V_2O_5 was sintered together with fly ash in the GM3 and GM5 samples the noticeably increase in the compressive strength were observed. The compressive strength is found to be > 67.42% and >103% with respect to the GM specimens for GM3 and GM5 samples respectively. Flexural and split tensile strength tests of geopolymer mortar samples with different percentage of pentoxide V_2O_5 were increased intensely with increasing content of V_2O_5 up to 5%, which is similar fashion in compressive strength improvement (**Fig. 4**). The percentage increment in flexural (22.65%, 74.69%) and split tensile strengths (34.13%, 111.2%) for GM3 and GM5 mortar samples in relation to GM mortar sample respectively.

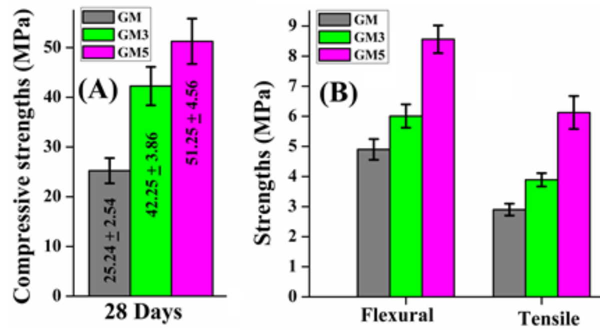

Fig. 4. (A) Compressive (B) Flexural and Tensile Strength.

The strengths improvement can be attributed to the following reasons. (1) Filler effect of interlocked needle shaped mullite as the fine particles fill the pores and hence make the denser structure with higher bonding with the geopolymer matrix. These fine particle materials play a vital role for the compaction of the geopolymer matrix (**Fig. 5B**). (2) The vanishing of the gas pores, and the stress occupying the pores eliminated at a certain V_2O_5 doping content [**19**]. (3) Main binding phase is aluminosilicate gel in geopolymeric network that provides inter-particle bonding, which further develops the macroscopic strength [**20-22**]. It evidences that the pentoxide V_2O_5 can improve the mechanical properties of geopolymer. Based on the above-mentioned results the amount of pentoxide V_2O_5 in fly ash can be used up to 5%, due to the reason that the GM5 mortar sample displays better results in terms of the strengths and durability.

The morphological analysis of geopolymer mortars by Field Emission Scanning Electron Microscopy (FESEM) are given in **Fig. 5B**. The formation of interlocked nano sized mullite in the matrices at 1000 ^oC are observed. When the percentage of V_2O_5 increases to 3% and 5%, more contents of mullite whiskers grow, therefore increases the V_2O_5 promotes the yield of whisker-shaped mullite. Generally, for the conventional fabrication method the mullitization temperature gives rise up to 1600 ^oC. When V_2O_5 introduces into fly ash due to its lower melting point (690 ^oC) it accelerates the formation of liquid phase and hence reduces the viscosity of silicate species in the matrix. The lower viscosity enhances the rate of reaction with other phases and more fast replacements and eliminations of the reaction products happen. Therefore the formation of the mullite whiskers and its anisotropic grain growth can be described by the lower melting point of secondary glass phase which enhances the precipitation of the mullite crystals in the geopolymeric matrix [**23**]. In the study [**24, 25**] determined that the incorporation of metal oxide reduced the viscosity of silica-rich liquid phase and hence mullitization temperature dropped intensely. During sintering of fly ash with V_2O_5 at 1000 ºC, mullite formation is controlled by diphasic aluminosilicate gels and dissolution–precipitation reactions.

During this reaction, aluminium oxide is dissolved in silica in this matrix up to its higher concentration [**26**]. Random mullite formation is observed in the high silica phase after attaining higher aluminium oxide concentration. After that the formation/growth of crystalline phase of mullite is controlled due to the dissolution activity of aluminium oxide in to the silica gel which is present in the geopolymer matrices.The characteristics of silica and aluminium oxide effects the formation-temperature of aluminium oxide dissolution velocity and the silica-rich liquid phase [**25**]. The metal oxide in terms of V_2O_5 exhibit the analogous character in the matrix while the fly ash sintered at typical temperature (<1000 ºC). Therefore, the presence of V_2O_5 dropped the temperature required for the mullite formation.

The EDX spectra of geopolymers mortar sample (GM5) are presented in **Fig. 5C**. The predominant elements are oxygen, aluminium and silicon. A little amounts of vanadium is also present. The major compounds are Al_2O_3 and SiO_2. The mullite formation phases in the matrix arises on sintering temperature in the alumina silicate (Al_2O_3–SiO_2) network. To confirm the phase transition in geopolymer mortar, the sample was investigated by X-ray diffraction (XRD) and are illustrated in **Fig. 5A**. Mullite peaks were appeared in the sample sintered at 1000 ºC with 5% V_2O_5, also the cristobalite peaks were noted. The samples reveal an almost complete mullitization process at this temperature. The alumino-silicate (mullite) phase reacts with alkaline solution to form a polycrystalline structure. During this phenomenon, dissolution rate and dimension of the Al-Si-O materials in a certain alkalinity effects on the final products. In this condition, fairly amount of nano dimension Al-Si-O materials are present and develop into a polycrystalline structure which act as reinforcement of the matrix [**27**]. It can be concluded that the lower activation energy of the reaction system and the enhanced reaction rate of Al_2O_3-SiO_2 to form mullite is possible in the existence of V_2O_5.

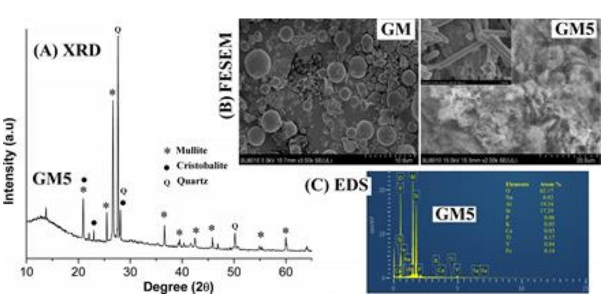

Fig. 5. Characterizations of geopolymer (A) XRD (B) FESEM (C) EDS.

Conclusion

Utilization of vast amount of fly ash has been explored with addition of V_2O_5 in concrete industry. In presence of alkaline activators, different concentration of V_2O_5 decreases the mullitization temperature (1000 ºC) to prepare a high-performance building composite in terms of higher durability as well as mechanical strength.

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Author's contributions

Muhammad Akbar Malik, Moumita Maiti, Manas Sarkar and Shilang Xu had conceived the plan. The experimental work and data analysis performed by Muhammad Akbar Malik, Moumita Maiti and Manas Sarkar. The paper has been written by Muhammad Akbar Malik under the supervision and guidance of Shilang Xu. Authors have no competing financial interests.

References

1. Taylor, M., *et al.*, **2006**.
2. Thongsang, S.; Sombatsompop, N.; Ansarifar, A., *Polymers for Advanced Technologies,* **2008**, *19,* 1296.
3. Dev, K.L.; Robinson, R.G., *International Journal of Geosynthetics & Ground Engineering,* **2015**, *1,* 32.
4. Ramesan, M.T., *et al., Chemist,* **2015**, *88,* 1.
5. Adak, D., Sarkar, M.; Mandal, S., *Construction & Building Materials,* **2014**, *70,* 453.
6. Xu, S., *et al., Construction & Building Materials,* **2018**, *164,* 238.
7. Zhang, H.Y., *et al., Construction & Building Materials,* **2014**, *55*, 38.
8. Gharzouni, A., *et al., Materials & Design,* **2016,** *94,* 221.
9. Maiti, M., *et al.*, **2018**, *3,* 1081.
10. Dong, Y., *et al., Journal of Alloys & Compounds,* **2008**, *460*, 599.
11. Park, Y.M., *et al., Materials Science & Engineering A,* **2007**, *454*, 518.
12. X. Huang, J.Y.H., B.C. Mutsuddy; *Ceramics International,* **1995**, *44*, 65.
13. Cabinets, M., *et al.*, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens) *1*. **2010**.
14. Astm, C., Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration; *Astm,* **1997**.
15. Neville, A.M., Properties of Concrete; 4th and Final Edition. **1995**.
16. ASTM C597–02 Standard test method for pulse velocity through concrete; *ASTM International, West Conshohocken.*
17. Li, J.H., H.W. Ma, and W.H. Huang, Effect of V2O5 on the properties of mullite ceramics synthesized from high-aluminum fly ash and bauxite; *Journal of Hazardous Materials,* **2009**, *166*, 1535.
18. Huang, K.S.; Yang, C.C., *Construction & Building Materials,* **2018**, *167,* 822.
19. Gupta, S., *et al., Energy & Fuels;* **2007**, *21,* 1052.
20. Palomo, A.; Grutzeck, M.W.; Blanco, M.T., *Cement & Concrete Research,* **1999**, *29,* 1323.
21. Rahier, H.; Vanmele, B.; Wastiels, J., *Journal of Materials Science,* **1996**, *31,* 80.
22. Duxson, P.; Lukey, G.C.; van Deventer, J.S.J., *Journal of Materials Science,* **2007**, *42,* 3044.
23. Wada, H., *et al., Journal of Materials Science Letters,* **1991**, *10*, 1076.
24. Hong, S.H., Cermignani, W.; Messing, G.L., *Journal of the European Ceramic Society,* **1996**, *16,* 133.

25. Kong, L.B., *et al.*; *Journal of Alloys & Compounds*, **2003**, *351*, 264.
26. Bartsch, M., *et al.*; *Journal of the American Ceramic Society*, **1999**, *30*.
27. Milheiro, F.A.C., *et al.*; *Ceramics International*, **2005,** *31*, 757.

