Review on supplementary cementitious materials used in inorganic polymer concrete

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Abstract: This paper presents a review on various supplementary cementitious materials generated from industries used in concrete, which one is considered a waste material. These materials are rich in aluminosilicates and are activated by sodium/potassium based alkaline solution to form geopolymer concrete. When these geopolymer concrete is used in civil engineering applications has showed better or similar mechanical properties and durability properties than ordinary Portland cement concrete. This paper also given the overview on sodium hydroxide (NaOH) & sodium silicate solution (Na₂SiO₃) ratios, curing adopted for different geopolymer concretes and the effect of adding fibres in geopolymer concretes.

1. Introduction
As the infrastructure requirement of the country is increasing every year, the utilization of the ordinary Portland cement (OPC) concrete is also increasing due to this the price of OPC is also increasing every year. During the manufacturing of OPC large amount of carbondioxide (CO₂) gases are released in to the atmosphere, which leads to the global warming. The alternative material for OPC concrete is geopolymer concrete. Geopolymer concrete can be manufactured by utilizing the wastes generated from industries and municipal solid waste. The industrial wastes used in geopolymer concrete are flyash, volcanic ash, metakaolin, red mud, ground granulated blast furnace slag (GGBFS), granulated corex slag (GCS), blast furnace slag (BFS), pulverized fuel ash (PFA), palm oil fuel ash (POFA), cement kiln dust (CKD). In India large amount of flyash is generated from thermal power plants. The only way to control the waste is to recycle or reuse. By using this industrial waste in concrete the problems due to landfills, groundwater contamination, air pollution and global warming effect can be reduced. The recent research works proved that the geopolymer concretes are similar or superior mechanical and durability properties than those of OPC concrete. This literature presents with the background to the needs for the development of alternative binders to manufacture concrete and the use of flyash and GGBS in concrete. The available literature on geopolymer concrete technology is briefly reviewed.

2. Study on geopolymer concrete manufactured from different industrial waste materials
Investigation carried out on the shear resistance of rectangular concrete beams reinforced with
three combinations of steel fibers and conventional stirrups by Narayanan et al. (1988)[30]. The tests have also been designed to study the effect of partial replacement of cement by pulverized fuel ash (PFA). The experiments have demonstrated the advantages of combining steel fibers and stirrups for shear reinforcement. The partial replacement of cement by PFA results in improved workability and higher long term strengths. Based on the test observations, a rapid method of assessing the ultimate shear strength of reinforced concrete beams containing both stirrups and fibres as shear reinforcement is suggested. Corelation has been obtained between observed test values and the predictions using the method suggested in this paper.

J.Davidovits (1991) [10]suggested when calcium hydroxide is replaced by metakaolin in the geopolymer concrete, workability of the concrete is reduced while compressive strength and flexural strength of the concrete increases with increase in sodium hydroxide concentration for metakaolin based geopolymer concrete with optimum sodium hydroxide concentration of 12M.

Davidovits et al. (1994)[11] reported that in the production of geopolymer about less than 3/5 of energy is required and 80–90% less CO₂ is generated than in the production of OPC. Thus, it is significance in environmental protection for the development and application of geopolymer concrete.

The production of cement is increasing about 3% annually McCaffrey (2002). The production of one ton of cement liberates about one ton of CO₂ to the atmosphere, as the result of de-carbonation of limestone in the kiln during manufacturing of cement and the combustion of fossil fuels Roy (1999).

Malhotra (1999)[25] the trading of carbon dioxide (CO₂) emissions is a critical factor for the industries, including the cement industries, as the greenhouse effect created by the emissions is considered to produce an increase in the global temperature that may result in climate changes. The “tradable emissions” refers to the economic mechanisms that are expected to help the countries worldwide to meet the emission reduction targets established by the Kyoto Protocol (1997).

Gengying et al. (2002)[18] suggested the influence on combination of flyash and ground granulated blast furnace slag (GGBFS) on the properties of compressive strength and resistance to sulfuric acid (H₂SO₄) attack, the results shown that the combination of flyash and GGBFS can improve both short-term and long-term properties of concrete, while high volume flyash concrete (HVFAC) requires a relatively longer time to get its beneficial effect.  
Investigation was carried out by Gourley et al. (2003)[19] on the usage of class F flyash. stated that the use of class F flyash was more preferable than class C flyash as source material to make geopolymers. The alkaline activators could be prepared by soluble alkali metals that are usually sodium (Na) or potassium (K) based.

Investigation was done to reduce the greenhouse gas emissions by Steenie et al. (2004). Reported the geopolymer concrete, a by-product material rich in silicon and aluminum, such as low-calcium (ASTMC class F) flyash, is chemically activated by a high-alkaline solution to form a paste that binds the loose coarse aggregates and fine aggregates and other un reacted materials in the mixture. The test results shown, the usage of geopolymer concrete is ecofriendly to the nature and reduces the green house gas emission.

Experimental investigation carried out by Djwantoro et al. (2008) [12]on the short term
engineering properties of geopolymer concrete. In this research, the influence of various parameters on the short term engineering properties of fresh and hardened low-calcium fly ash based geopolymer mortar were studied.

According to Yang et al. (2008)[38] much higher compressive strength is developed in GGBFS based alkali-activated mortars than flyash based mortars. The rate of compressive strength developed for GGBFS based alkali activated mortars was more notable at early age on the other hand, compressive strength of fly ash based alkali activated mortar sharply increased with increase in age.

In order to produce the high strength geopolymer concrete Bakri et al. (2010) [29]suggested flyash and GGBS based geopolymer concrete, which is having early setting time and compressive strength. Compressive strength increases with flyash fineness and thus reduction in porosity obtained. The use of GGBS significantly increases the setting time and compressive strength. Kaisuda somna et al. (2011) [37]suggested the compressive strength of ground flyash curied under ambient temperature by varying the sodium hydroxide (NaOH) concentration in between 4.5molar (M) to 16molar (M). When the concentration of NaOH was increased from 4.5M to 14M the compressive strength increases. The increase in compressive strength of samples is due to higher amount of silica & alumina content in the ground flyash upon further increase in the NaOH concentration from 14M to 16M the compressive strength of the ground flyash of hardened geopolymer concrete decreases.

Investigation on the influence of the superplasticizer and sodium hydroxide (NaOH) concentration on the geopolymer concrete was carried out by Fadhil et al. (2011)[14]. Found out that low superplasticizer content had poor filling and passing ability. Superplasticizer dosage up to 6% contributed to passing ability and workability further increase in dosage does not contribute any change. As the NaOH concentration increases from 8M to 14M compressive strength of geopolymer concrete increases but further increase in concentration of NaOH solution compressive strength of geopolymer concrete decreases.

Ganupati Naidu P et al. (2012)[17] suggested the compressive strength of geopolymer concrete increases with increase in GGBS percentage in concrete by replacing flyash content up to 30% and also found 90% of the compressive strength was achieved in 14 days.

Andri Kusbiantoro et al. (2012)[6] to attain the required strength in geopolymer concretes three different curing regimes, ambient curing at 35°C, exposure curing at 55°C, and oven curing at 65°C for 24hours. Among all the curing methods oven curing is found to be best in attaining the strength for geopolymer concretes. It is also identified that 7% replacement of flyash by rice husk ash found to have best compressive strength results for the suggested curing conditions.

Aydins et al. (2012)[8] studied the effect of steam curing and autoclave curing on the compressive strength of geopolymer concrete mixes. Ground granulated blast furnace slag with low hydration modulus of 1.33 was activated with sodium based alkaline solution in different proportions. The aggregate to blinder & water to blinder ratio was fixed to 2.75 and 0.44 for all the mixtures. One batch of specimens were kept in humidity cabinet for 5 hours before they are subjected to steam curing for 5 hours at a temp of 80°C. Another batch of specimens were kept in humidity cabinet for 24 hours before they are subjected to autoclave curing at 210°C for 5 hours and 2 Megapascals (Mpa) pressure was maintained. Compressive strength of alkaline activated slag was higher, when cured under steam curing than the Portland cement.
motor. The compressive strength was achieved in between 15-19Mpa under autoclave curing. High performance alkaline activated slag motors with compressive strength 70Mpa can be achieved using 2% Na$_2$O by weight of slag. The major conclusion drawn autoclave curing is more favorable for alkali activator slag with low Na$_2$O concentration.

Experimental work was conducted to find the optimum mix for the geopolymer concrete by Abdul et al. (2012)[1]. Suggested geopolymer concrete utilizes an alternate material including flyash as binding material in place of cement. When flyash reacts with sodium based alkaline solution to form a gel which binds the fine aggregates and coarse aggregates. An attempt has been made to find out an optimum mix for geopolymer concrete. Concrete cubes of size 150mm x 150mm x 150 mm were prepared and cured under steam curing for 24 hours. The compressive strength was found out at 7 days and 28 days.

He jiey et al. (2013) [21]suggested the effect of curing and varying concentration of sodium hydroxide (NaOH) solution on compressive strength of geopolymer pastes prepared from industrial waste products such as rice husk ash & red mud. The higher concentration of NaOH in the geopolymer paste resulted decrease in the compressive strength. The ratio of rice husk ash/ red mud was fixed to 0.4. The geopolymer paste was activated at 4M NaOH after casting the specimen were left to cure at room temperature and atmospheric pressure for the period of 14, 28, 35, 42, and 49days before subjected to compressive strength test. At the 35th day of curing the compressive strength was found to be 11.7Mpa at this age the complete geopolymerization takes place. Geopolymerization is slow in the case of flyash & rice husk ash, when compared with other industrial wastes such as flyash and metakaolin.

Study was conducted on copper mine tailings, cement klin dust, reagent grade 98% sodium hydroxide (NaOH) by Ahmari et al. (2013) [3] and found the addition of cement klin dust to geopolymers resulted in improvement of compressive strength as well as durability characteristics.

Investigation was carried on the Influence of iron making slags on strength and micro structure of flyash geopolymer by SK Nath et al. (2013)[36]. The materials used in this work are flyash, granulated blast furnace slag, granulated corex slag (GCS) and 6M sodium hydroxide (NaOH) solution. Out of the two iron making slags, when granulated corex slag is mixed with flyash is found to be better with maximum strength developed of 93.4 Mpa.

The combination of ground granulated blast furnace slag (GGBFS) with class F flyash can have a significant effect on the setting time and compressive strength development of geopolymer concrete. The effect of different proportions of GGBFS and activator content on the workability and strength properties of flyash based geopolymer concrete was studied by the Partha et al. (2014)[34]. The test result shown that 28-days compressive strength reached up to 51 Mpa in geopolymer concrete containing 20% slag, 80% flyash and 40% activator solution with sodium silicate/sodium hydroxide ratio of 1.5 when cured at 20 °C.

Moruf olalekan et al. (2014)[28] suggested by using the materials steel slag and palmoil fuel ash, sodium hydroxide and sodium based alkaline solution the cubes casted and cured under oven curing at 60°C for 24 hours. The maximum strength of 57.1Mpa was observed with 10M sodium hydroxide (NaOH) concentration and also around 80% 28days strength obtained in 3days.

David Wiyono et al. (2015)[13] suggested in his study only volcanic mud is treated to improve its properties while flyash has its improved properties. According to ASTM C 618-05 it states that volcanic
mud can be classified as pozzolonic material due to its higher percentage of SiO₂, Al₂O₃, and Fe₂O₃. As per standards of conventional concrete, fails under immersion of 10% sulfuric acid for 90 days while high volume flyash (HVFA) concrete specimens shows excellent performance without pozzolanic content. In terms of mass loss, high volume sidoarjo mud (HVSM) performs significantly better than conventional concrete because of addition of geopolymer as an accelerator. HVSM specimen which in turn increases durability than HVFA concrete specimens. An initiative may be made to replace 50% concrete usage with fly ash and volcanic mud which are not harmful to environment.

Steel reinforcement in the ordinary Portland cement (OPC) concrete causes corrosion & changes its mechanical properties, when it is subjected to adverse temperature & fire conditions. To control this Xiaochen Fan et al. (2016)[18] used inorganic polymer concrete (IPC) reinforced with basalt rebar’s. IPC manufactured with flyash & ground granulated blast furnace slag and activated with alkaline solution. The mechanical properties of the IPC were measured and compared with OPC concrete. The flexural behaviour of basalt reinforced IPC beam were investigated and compared with the steel reinforced OPC beam the results indicated that elastic modulus of IPC was very close to OPC while the compressive strength of IPC were around 80% of those of OPC. The crack patterns of basalt reinforced IPC beam is almost similar to the steel reinforcement OPC concrete, but the maximum crack width of basalt reinforced IPC is 2 times the OPC concrete beam.

3. Studies on artificial aggregates used in geopolymer concrete

Nitendra palankar et al. (2015)[32] suggested that ground granulated blast furnace slag & flyash based geopolymer binder has higher compressive strength when compared with ordinary Portland cement concrete mix. In this paper research was conducted on slag based aggregates in the geo-polymer concrete. The percentages of slag based aggregates used in the study are 0%, 25%, 50%, 75% and 100% by volume. When these slag based aggregates are used in the GGBFS & FA based geopolymer mixes, recorded slightly lower fresh and mechanical properties upon comparing with natural aggregates due to presence of calcite on the surface of slag aggregates. Due to the presence of porus structure on the steel slag course aggregates, higher the water absorption and volume of permeable voids. This also addressed partial solution for disposal of steel slag and make useful for construction.

A.Akbarn ezhad et.al (2015)[2] suggested using the construction and demolition waste in concrete as aggregates. By varying the percentage of recycled geopolymer aggregates (RGA) and recycled course aggregates (RCA). The results represented that the water absorption for 24 h was much higher for RGA than natural aggregates (NA) & RCA. The oven dry bulk density is more for RGA upon compared with NA & RCA. The compressive strength, modulus of rupture and modulus of elasticity is more when RGA is replaced with NA. These values are more when compared with the RCA. This shows that the RGA are the potential use for concrete.

4. Studies on hybrid fibre geopolymer concrete

Eswari et al. (2008)[4] did an experimental investigation on the ductility performance of hybrid fibre reinforced concrete. The influence of different volume fractions of fibre content on the ductility performance of hybrid fibre reinforced concrete specimens is investigated. The hybrid fibre reinforced concrete specimen’s exhibit enhanced strength in flexure. The hybrid fibre reinforced concrete specimens exhibit increase in deflection comparison with plain concrete. The hybrid fibre reinforced concrete specimen’s exhibit reduced crack width at all load levels. The effect of hybrid fibres on the strength and behaviour of high performance concrete beam column joints subjected to reverse cyclic loads was studied.
Ganesan et al. (2014)[16] Addition of fibres in hybrid form improved many of the engineering properties such as the first crack load, ultimate load and ductility factor of the composite. The combination of 1% volume fraction of steel fibres and 0.15% volume fraction of polypropylene fibres gave better performance with respect to energy dissipation capacity and stiffness degradation than the other combinations.

John Bruston et al. (2016)[1] suggested when plain concrete is subjected to tensile stress, cracks are developed, to bridge these cracks fibers are uniformly distributed in concrete. Addition of fibers in the plain concrete develops the mechanical behavior of concrete. The advantage of steel fiber in concrete are improved flexural toughness, flexural fatigue, endurance and impact resistance. But the addition of steel fibre increases dead load, reduced workability and fire balling at high dosages and susceptibility to corrosion. For these reason basalt fiber is the alternative fiber for concrete reinforcement application due to its excellent mechanical properties and environment friendly. In this paper it was suggested that usage of fiber beyond 12kg/m$^3$ of basalt fibre (BF) & 40kg/m$^3$ of minibars (MB) fibres causes bracing effect. The addition of basalt fibre improves the first crack strength in flexural loading and higher strength is obtained by using longer 50mm BF than 36mm BF. A dosage of 12kg/m$^3$ of 50mm BF have higher first crack strength than 40 kg/m$^3$ of steel fibre. The addition of MB fiber in the concrete increased the first crack strength in both the flexure & impact loading further increase in the dosage strength increases. The result indicated both types of fiber increases pre-cracking strength but only the minibars enhanced the post cracking behavior likely due to protection from the polymer.

5. Summary of review

Geopolymer concrete in structural applications has led to the total elimination of cement from concrete, which ultimately becomes “Green concrete”. The compressive strength of geopolymer concrete increases with increase in the concentrations of NaOH up to 14M and further increase in NaOH concentration the compressive strength decreases. Addition of fibres in the geopolymer concrete helps in arresting the cracks and improves the mechanical and durability properties. Industrial wastes once considered as a waste material can be put into useful material by using in geopolymer concrete. Ultra high strength geopolymer concrete can be obtained by adding silica fume, quartz sand and quartz powder. Strength of geopolymer concrete depends on curing conditions.

6. References

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