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Physicochemical Propertiesof Alkali Activated Fly Ash Based Geopolymer Concrete: A Review

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Abstract: Geopolymer is a term covering a class of synthetic alumino silicate materials with potential use in a number of areas, essentially as a replacement for Portland cement. Geopolymer is a lower carbon dioxide production emission, greater chemical and thermal resistance with better mechanical properties. In this paper a in depth review on alkali activated geopolymer was made, starting from its evolution till recent development. These technology which uses alkali activated binder instead of cement will emerge as the future. But still lot of studies and research were needed in finding the right way of curing for achieving the desiredstrength and also the effect of alkalinity on rebars and concrete ages.

Keywords: *Geopolymer, Flyash, Alkali activated binder, polymer concrete*

Introduction

Without cement and concrete there is no creativity in the world. The global prespective is "Greenhouse emission". To avoid carbon dioxide emission throughout the world, the alternative binders can be used to fulfill the need of cement. So there is a urgent need for alternative binders to compromise our requirements and infra structures without CO_2 level. Due to this reason some alternative binder are to be used. Geopolymer is considered as the latest trend after lime and Portland cement. It is also called as carbon negative cement. The geopolymer is also commonly used for to as Inorganic polymers, alkali – activated cements, Geocements, alkali bonded ceramics, hydroceramics etc.

In geopolymer Technology aluminosilicate materials such as kaolinite, feldspar and industrial solid residues such as flyash, metallurgical slag, mining wastes etc were used as raw materials. The main source materials of geopolymer are low water demand. So it is able to release aluminium easily. The main alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na2sio3) and potassium silicate (K2SIO3) are used to activate alumino silicate materials. In the above material KOH have high level of alkalinity.

Geopolymer is generally more durable and stronger than that of metakaolin based geopolymer. The slag based geopolymer have high early strength and greater acid resistance than metakaolin and flyash based systems. [1]

Precursor of Geopolymerisation

In 1970's the French chemical Engineer Davidovits interest in this area with the development of alkali – activated binders based on metakaolin and coined the term geoploymer. It is good in fire resistance and high early strength. He studied the charecterisation of geopolymer properties and applications.

In 1980's and 1990's geopolymer institute was hosted in france and Australia. Davidovits has continued the geopolymer technology as a subset of alkali activated materials technology through thus institute. This geopolymer concrete was achieved early compressive strength of 20MPa within 4hours with a low temperature.

In 1991 geopolymer was used in military runway. Later 1993, it was used in industries as well as military installations. This concrete will fulfill the performance, cost reduction and lower CO_2 emissions. [2]

The activator in geopolymer is alkali metal hydroxide or silicate low calcium flyashes and calcined clays were used in geopolymer Technology, geoploymer have highest Al and lowest Ca concentration. The geopolymer contains high ceramic properties. This polymerization have involves the chemical reaction of alumino-silicate oxides with alkali ploysilicates Si-O-Al bonds. This is a new generation alkali material which is used as filler.

Mostly, works on Geopolymer have been based on a precursor derived from class F fly ash got by burning bituminous coals. Even class C fly ash which is derived from burning lignite and subbituminous coals in the thermal power stations is also used in the manufacture of Geopolymer mortar/concrete in which Geopolymeric gel and calcium silicate hydrate gel co-exist. To dissolve the silica and alumina ions in the precursors, highly alkaline solutions are needed to process Geopolymerisation (Prof.JosephDavidovits, 1994); The alkaline activators such as sodium hydroxide (NaoH), potassium hydroxide (KOH), sodium silicate (Na_2Sio_3) and potassium silicate

(K_2Sio_3) were used as activators for aluminosilicate reaction. [3]

Comparision between Geopolymer and ordinary Portland cement concrete

Geopolymer concrete has lower impact on global warming them ordinary Portland cement concrete. Geopolymerisation has definitely a good potential for the production of green concrete and construction materials with lower carbon foot print. The environmental impact of geopolymer has to be quantified by considering the impact of the waste products used through life cycle assembly. [4, 5, 6]

The concept of life cycle system is

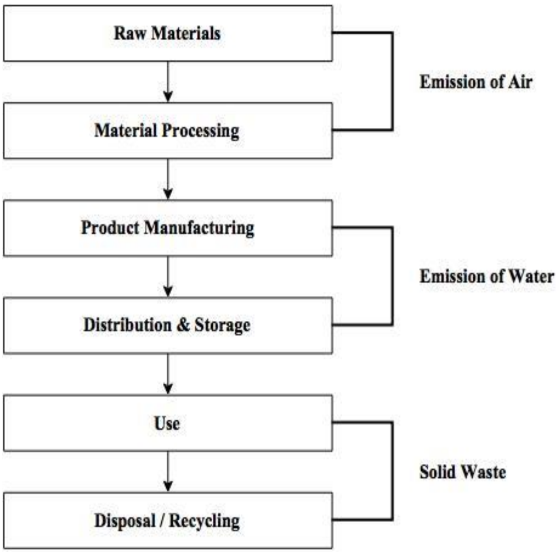


Fig.1 *life cycle system*

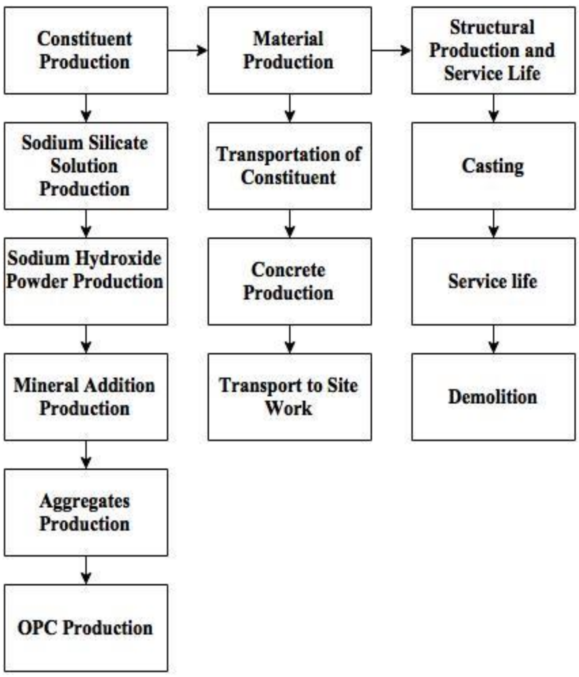
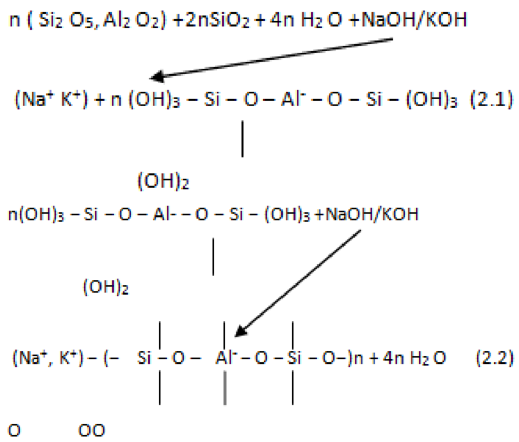


Fig.2 *Description of Geopolymer concrete Life cycle*

Due to the lower CO2 in geopolymer concrete with the use of sodium silicate solution as activator that results shows the pollution transfer within all other environmental impact catagories. The geopolymer concrete raw materials having Si/Al molar ratio which gives as industrial waste and does not have allocations impact. But in geopolymer technology used waste by-product materials iron and ferro-nickal slags cannot be used in the normal OPC, but it can be used as geopoymeric binders. Slag based geopolymer concrete requires small amount of sodium silicate and therefore has low environmental impact. So it reduces environment foot print in the sustainable for the future. [7]

Present Scenario of geopolymer

Several alternate binders are there such as alkali-activated cement, calcium sulpho aluminate cement, magnesium oxy carbonate cement, super sulphated cement etc are being made with the advantage of Portland cement. In recent years geopolymer has drawn greater impact among these binders because of its early age compressive strength, low permeability, good chemical resistance and excellent fire resistance. In recent days a considerable development in alkali-activated cement and is classified based on a phase composition of the hydration products. R-A-S-H (R = Na+ or K+) in the aluminosilicate based systems and R-C-A-S-H in the alkali-activated slag or alkali Portland cements. Geopolymer is used to develop various building materials, concrete, fire resistant coatings, fibre reinforced composites and waste immobilization solutions for the chemical and nuclear industries. The schematic formation of Geopolymer material is described in Equations 1 & 2.



It can be seen from the last term in Equation (2) that water is released from the Geopolymer matrix during chemical reaction. It is important to note the role of water in the formation of Geopolymers. This water, expelled from the Geopolymer matrix during curing and further drying periods, leaves discontinuous nano-pores in the matrix which are beneficial to the performance of Geopolymers. It imparts only workability to the mixture during handling and in no way plays any role in the chemical reaction that takes place, which is in contrast to the chemical reaction that takes place with water in a Portland cement mixture during the hydration process (Hardjito&Rangan, 2005);

Geopolymer concrete properties

The behavior and compressive strength of reinforced geopolymer concrete are similar to Portland cement concrete. It also have good resistance to sulfate attack, acid resistance, creep and drying shrinkage. The bond characteristics of geopolymer concrete have comparatively high when compared to Portland cement concrete [9]. The design provision for shear and bond strength for reinforced flyash based geopolymer is available in building codes and standards. The mechanical properties for geopolymer concrete have good durability and fire resistance. This technology can used in marine environments, environment with high carbon dioxide or sulphate rich soils, mining, industries, sewer systems and railway sleepers in main line tracks and also good resistance in wall panel to fire. The main property is high early strength and fast setting [8].

Application of flyash based geopolymer concrete

Geopolymer is a good alternative binder for ordinary portland cement

- Geopolymer is a more durable concrete when compare to ordinary Portland cement
- It is also manufactured sewer pipes, wall panels, culverts, precast units etc.
- It have high compressive and flexural strength, lower drying shrinkage, resistance to sulphate attack and acid attack
- Geopoloymer have more tensile strength when compared with ordinary Portland cement. So minimum steel is required and also there is no brittle in concrete.
- Geopolymer more suitable in under water structures due to early strength and rapid setting.
- Geopolymer also suitable for quick repair and rehabilitations structures.
- Geopolymer have high abrasion resistant concrete [11].

Limitations of geopolymer concrete technology

Still geopolymer is under developing stage only due to the limitations some of the limitations are

- Maintaining the homogeneity in the source materials such as flyash and alkaline materials is difficult
- The preparation of alkaline activator solutions is difficult due to the mixing proportions.
- The major limitation is curing. The curing was done by steam or dry curing. The utilization is very difficult.
- Cost of alkaline solution is high. The mixing of alkaline solution is to be prepare together at 24 hours prior to use.
- Alkalinity gives hazards to the health.
- There is no availability of specifications and guidelines.
- Care should be taken while preparing mix design and mixing the materials.
- It is not a user friendly for preparing and curing.[11]

Works on Geopolymer concrete

There were huge number of research studies going on geopolymer concrete and GC based construction products were gaining importance. In this section some studies were presented in order of work and were discussed.

The latest papers on Fiber reinforced geopolymeric composites(FRGCS) [19] are reinforced with polypropylene fibers which have boosted compressive strength, tensile strength , flexural strength ,impact and toughness capacity well above the Fiber reinforced concrete(FRCCs). Fiber reinforced geopolymeric composites(FRGCS) which is found much greener and durable than the cement replaced composition of concrete (FRCCs). Fly ash based geopolymer concrete has been successfully replaced fractions of aggregate with industrial and agricultural waste like limestone and oil palm shell (OPS)has improved the engineering identify with high mechanical and betterment in fresh properties. [20] Binder replacement techniques using kaolinite & silica fume has also boosted the mechanical strength and durability of geopolymer concrete [21].Prominent variations in geopolymer concrete in strength and fresh properties has been spotted with the degree of heating and the concentration of sodium hydroxide[22]. The study on carbon dioxide reduction factor in alkali activated concrete with bench marking the normal OPCconcrete and also with GGBS replaced the cement binder showed considerable reduction of the greenhouse gas [23].Investigating into the fracture behavior of geopolymer concrete with that of the conventional concrete divulged that the structural failure of the geopolymer is more brittle when compared to that of the ordinary concrete [24]. Experimental study on the effective usage of bottom ash (BA) and metakaolin (MK) in geopolymer mortar is also a confirmed method in improving the engineering properties of the geo polymer concrete.[25].Alkali-activation of fly ash added with aluminum powder blowing agent led to the synthesis of inorganic fly ash-based foam (FAF) (14). The FAF is characterized by its compressive and flexural strength, thermal conductivity and capacity, exposure to high temperatures.

Fresh and hardened concrete

(Hardjito et al, 2005); [2] conducted experiments to study the materials and the mixture proportions, the manufacturing process and the influence of various parameters on the properties of fresh and hardened Geopolymer concrete. The fly ash-based Geopolymer concrete had excellent compressive strength which might be suitable for structural applications. It was found that fresh Geopolymer concrete can retain its workability to 120 minutes after mixing, without setting or without degradation in compressive strength. With regard to hardened concrete, the molar ratio of H2O-to-Na2O significantly influenced the compressive strength of fly ash-based Geopolymer concrete. An increase in this ratio decreased the compressive strength.

Other important factors that influenced the properties of hardened fly ash-based Geopolymer concrete were the curing temperature and the curing time. The higher the curing temperature, the higher was the compressive strength. The fly ash-based Geopolymer concrete also showed excellent resistance to sulphate attack, underwent low creep, and suffered very little drying shrinkage.

Relationship between NaOH & KOH

NaOH	KOH
In NaoH solution is observed more Al and Si	In KOH solution produces geopolymers with a high mechanical strength
Al-Si minerals have high CaO content	In KOH, Al-Si is lower
It have low compressive strength when compared to KOH	It have high compressive strength when compared to NaOH
The cracking is more when compared to KOH	The addition of KOH is benefit of compressive strength and reduce the occurrence of cracking

Durability of Geopolymer Concrete

Acid Attack

Suresh Thokchom et al, 2009);[12] investigated and expressed that fly ash based Geopolymer mortar specimens manufactured with varying alkali content showed varying degree of deterioration when exposed to sulfuric acid. Though mortar specimens revealed no visible signs of structural disintegration, surface deterioration was clearly visible under an optical microscope and these appeared to be severe in specimen manufactured with lesser alkali content.

Sulphate Attack

(Bakharev, 2005); [13] has investigated and presented this paper about the durability of Geopolymer materials manufactured using class F fly ash and alkaline activators when exposed to a sulphate environment. Three tests were used to determine resistance of Geopolymer materials. The tests involved immersions for a period of 5 months into 5% solutions of sodium sulphate and magnesium sulphate, and a solution of 5% sodium sulphate+5% magnesium sulphate. The evolution of weight, compressive strength, products of degradation and microstructural changes were studied. In the sodium sulphate solution, significant fluctuations of strength occurred with strength reduction. The mixture of sodium hydroxide and sodium silicate as activators, while the strength was increased. In the magnesium sulphatesolution, the strength was increased respectively. The most significant deterioration was observed in the sodium sulphate solution and it appeared to be connected to migration of alkalis into solution. In the magnesium sulphate solution, migration of alkalis into the solution and diffusion of magnesium and calcium to the subsurface areas was observed in the specimen's prepared using sodium silicate and a mixture of sodium and potassium hydroxides as activators. The least strength changes were found in the solution of 5% sodium sulphate+5% magnesium sulphate. The material prepared using sodium hydroxide had the best performance, which was attributed to its stable cross-linked aluminosilicate polymer structure.

Geopolymer concrete with marine environment

(Reddy et al., 2011);[14] have focused their study to evaluate the durability characteristics of low calcium fly ash based Geopolymer concretes exposed to marine environment and comparison with ordinary Portland cement concrete under similar exposure was made. To achieve this goal, 8 and 14Molar Geopolymer concrete (GPC) and Ordinary Portland Cement Concrete (OPC) mixes were prepared and tested for exposure in seawater. The test results indicated that the GPC have shown excellent resistance to chloride attack, resisting longer time to corrosion cracking when compared to OPC concrete. Therefore, by analyzing and comparing the behaviour and properties of both concretes, it was observed that the low calcium fly ash-based Geopolymer concrete was more homogeneous and well-bonded to the aggregate than ordinary Portland cement concrete. Consequently, better crack resistance and long-term durability were obtained with GPC concrete. The effect of age on the strength of the Geopolymer mixtures was different from those of the OPC. It was found that the strengths were acquired more quickly with Geopolymer concretes. The electrical resistivity and permeability of the low calcium fly ash-based GPC were not drastically affected by the severe marine environment in view of reduced cracking.

Bond Strength of Geopolymer Concrete

(Smith Songpiriyakij et al., 2011); [15] have presented in their paper about the bonding strength between the embedded rebar and substrate concrete by using Geopolymer paste as the bonding agent. The bonding strengths of round bar and Geopolymer pastes were slightly higher than that of control concrete. The strength was notably high in case of deformed bars. In comparison with commercial repair materials, the bonding strengths of Geopolymer paste were higher than those of epoxies.These tested results indicated that the bonding strength due to

Geopolymer paste was high enough and possibly could be used as bonding material for repair works. The mixtures containing high silica fume content and high NaOH concentration were recommended to enhance both compressive and bonding strengths. The results of compressive and bonding strengths indicated that Geopolymer paste with 60% fly ash and 40% silica fume with 18M NaOH concentration gave the highest compressive and bonding strengths. The use of rice husk ash incorporation with fly ash as the starting materials could be developed for high compressive and bonding strengths but the curing time must be longer – that is 28 days. Also, use of fly ash incorporation with silica fume enhanced the compressive and bonding strengths of the Geopolymer paste significantly. The higher the quantity of silica fume, higher was the compressive and bonding strengths. The higher value of compressive and bonding strengths was obtained for 18M concentration of NaOH indicating the effect of alkaline concentration.

Thermal Properties of Geopolymer Concrete

(Daniel & Jay Sanjayan, 2010); [16] presented after an extensive research done on the effect of elevated temperature on Geopolymer paste, mortar and concrete using Australian fly ashes as precursors. Geopolymer was activated by sodium silicate and potassium hydroxide solutions. Various experimental parameters have been examined such as specimen sizing, aggregate sizing, type of aggregate and type of superplasticiser. The study identified size of specimen and aggregate had influenced the thermal behaviour at elevated temperature of 800°C. Aggregate size greater than 10 mm resulted in good strength performances in both ambient and elevated temperatures.

The compressive strength of geopolymer concrete cubes

The highest strength was performed by geopolymer concrete cubes when compared to ordinary Portland cement. If when the molarity increases, the compressive strength of geopolymer concrete was also increased.

Split Tensile Strength

The tensile strength of geoploymer concrete was very high when compared to OPC. If molarity increases the tensile strength of geoploymer was also increased.

(Chang EeHui, 2009);[17] has focused on the importance of shear and bond behaviour of reinforced low calcium fly ash-based Geopolymer concrete beams. For the study of shear behaviour of Geopolymer concrete beams, a total of nine beam specimens were cast. The beams were 200 mm x 300 mm in cross section with an effective length of 1680 mm. The longitudinal tensile reinforcement ratios were 1.74%, 2.32% and 3.14%. The behaviour of reinforced Geopolymer concrete beams failing in shear, including the failure modes and crack patterns, were found to be similar to those observed in reinforced Portland cement concrete beams. It was also found that the methods of calculations, including code provisions, used in the case of reinforced Portland cement concrete beams shall be applicable for predicting the shear strength of reinforced Geopolymer concrete beams.

Reinforced Geopolymer Concrete Columns

(Rahman Muhammed, 2011);[18] has investigated the failure behaviour of the Geopolymer concrete columns under biaxial loading and compared with that of OPC concrete columns. Strength of the columns was calculated using the well-known Bresler's load reciprocal formula and the current Australian Standard for OPC concrete. Bresler's formula which is commonly used for the design of OPC concrete columns resulted in good correlation with test results of the Geopolymer concrete columns.

Authors Study

The authors had studied about some basic properties of geopolymer concrete for their research work and these studies shows the following results.

Based on the investigation the following conclusions were drawn.

- The utilization of geopolymer as cementious material provides additional environmental as well as technical benefits. The geopolymer technology reduces the cost of making concrete and increases its strength and durability characteristics.
- The initial setting time of flyash based geopolymer binding material is higher upto 75% when compared with OPC; however the final setting time is almost similar.
- The setting time is achieved only through elevated atmospheric temperature of around 65◦C, hence it was concluded that heat curing is the possible way of curing geopolymer concrete.

Figure 3 *Shows Slump Cone test on geopolymer concrete*

Figure 4 *Shows Flow table test on geopolymer concrete*

Figure 5 *Shows Compression test on geopolymer concrete*

- The strength of mortar cubes increases the maximum of 75.86% on third day when compared to OPC specimens. The increase in strength reduces as the age increases, hence it is concluded that the maximum strength o geopolymer mortar cube was achieved in its early ages.
- The workability of geopolymer concrete is less than OPC concrete. The workability decreases with increases in concentration of NaoH but false within the allowable limit.
- The slump cone value for geopolymer concrete lies between 80 to 100mm. The slump value o M30 and M50 is maximum and G30-12M and G50-12M is minimum. All mix shows the true slump behavior during testing.
- The flow table value reduces upto 24% in G40-12M mix when compared to M30 and 34.57% in G50-12M when compared to M50, hence it was concluded that higher NaoH concentration and higher grade of geopolymer concrete affects the flow properties.
- The results of compressive and split tensile strength have indicated that the strength have indicated that the strength of geopolymer concrete increases with respect to NaOH concentration. Further G30-8M and G50-8M has higher strength when compared to M30 and M50 respectively.
- The results of compressive and split tensile strength of G30 and G50 specimens were maximum during early ages. Due to faster hydration, the strength normalizes on later ages. The maximum value of compression and splitting strength is observed in G30-12M and G50-12M on all ages.

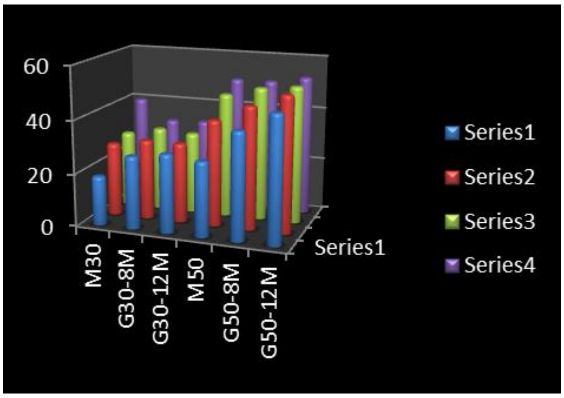


Figure 6 *Results on compressive strength of OPC and Geopolymer concrete*

- There was about 37.8% increases in flexural strength for G30-12M geopolymer concrete when compare to M30 and 28.7% increase in flexural strength for G50-12M when compared with M50. The reason for increases in flexural strength was lesser internal voids and lesser capillary channel in geopolymer column.
- The results of ultrasonic pulse velocity have indicated that all geopolymer specimens have excellent quality. The G30-12M and G50-12M have higher pulse wave velocity when compared with normal OBC specimen.
- The increase in pulse wave velocity was 3.24% for G30-12m specimen and 1.35% for G50-12M specimen.
- Water absorption of geopolymer concrete column having lower water absorption when compared with OPC specimen. The lowest value of water absorption is observed at G50-12m and G30-12M respectively.
- The G50-12M specimen has 27% lesser water absorption when compared to M50 and G30-12M has 40% lesser absorption when compared to M30. The lower water absorption is due to denser micro structural bond in geopolymer concrete.
- The geopolymer specimen exposed to 5% of chloride solution for 4 weeks and 8 weeks losses its mass. The maximum loss is observed in OPC specimen when compared with geopolymer specimen.
- The G30 specimens had lost its mass by 1.87% after 4 weeks and 3.6% after 8 weeks. Similarly the G50 specimen showed a loss of 1.2% after 4 weeks and 2.5% after 8 weeks.

- Geopolymer concrete cubes exposed to 5% of sodium sulphate solution showed no visible sign of surface erosion, cracking or spalling of specimen upto 4 weeks and little erosion are noticed after 4 weeks.
- The increase in mass of specimen soaked in sodium sulphate solutions was approximately 1.2% after weeks and 1.72% after 8 weeks of exposure.
- OPC specimen soaked in sodium sulphate solution shown an increase in mass which was about 4.63% after 8 weeks of exposure which is higher than geopolymer mix.
- Exposure of heat cured flyash based geopolymer concrete specimens to sodium sulphate solutions had strength loss of about 6.26% for G30 and 4.99% or G50. But in OPC concrete the changes is compressive strength was about 13.89% for M30 grade and 8.76% for M50 grade after 8 weeks of exposure.
- Geopolymer concrete cubes exposed to concentrated sulphuric acid exhibited marginal weight loss o 1.70% Initial and weight loss of 20.43% was noticed after 8 weeks of observation. On the contrary OPC specimen had weight loss of 50% after 8 weeks of exposure.
- All geopolymer concrete specimen exposed concentrated sulphuric acid has lesser surface erosion. When compared to OPC specimen, hence geopolymer concrete is more resistive towards adverse condition.
- In rapid chloride penetration test the presence of sodium hydroxide in the geoploymer specimen produced more heat which started melting and collapsing the test setup. This has proved that RCPT could not be done on geopolymer concrete specimen due to its high alkalinity and low conductivity of current.

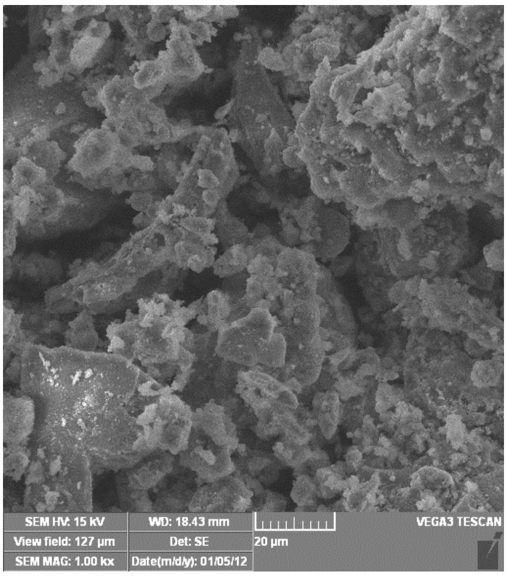


***Figure 7** SEM image of a typical geopolymer concrete*

- The SEM image in Figure 7 shows the micrograph of a geopolymer concrete with 12 molarity and shows good structural bon as that of a cement concrete

Conclusion

This chapter presented the studies done on geopolymer concrete and its effective utilization in building industry. From the studies it is evident that the geopolymer can act as the perfect replacement for cement based concrete industries. The geopolymer study presented in this chapter is limited to flyash based geopolymer; further there were many studies going on various monomer materials like metakaoline, calcined clay etc. This complete replacement of cement has a capability of reducing CO2 emission.

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