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Durability of fly ash based geopolymer concrete in the presence of silica fume

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ABSTRACT

Geopolymer is a green cementitious material and has excellent mechanical properties, low energy in its production and emits less carbon dioxide. In this paper, the effect of silica fume on durability properties of fly ash based geopolymer concrete have been investigated by immersing the cubes in 2% sulphuric acid and 5% sodium chloride solutions. The resistance of specimens to chemical attack was evaluated visually, measuring change in the weights and percent losses in compressive strength at different intervals of time. A control mix was also cast as M40 with ordinary Portland cement concrete for comparison. Percent losses in compressive strengths in the case of control (M40) and GPC3 in 2% H_2SO_4 at 90 d were found 36 and 8%. Percent losses in compressive strengths in the case of control (M40) and GPC3 in 5% NaCl at 90 d were 18% and about 0%.Thus the resistance of geopolymer concrete incorporating silica fume in sulphuric acid and chloride solution was significantly higher than that of the control.

1. Introduction

Concrete is a material that is used for many purposes in construction and does not need maintenance during the life-time of the structure. Concrete structures made from Portland cement, when exposed to aggressive environments; tend to deteriorate much faster than their expected service life (Mehta and Burrows, 2001). Durability of OPC concrete is connected to the properties of its constituent ingredients such as $Ca(OH)_2$ and calcium silicate hydrates. Deterioration may take place due to number of chemical reactions occurring between the aggressive environment and calcium containing components of the concrete. The reactions between the acidic effluent and cement hydrates produce calcium salts which may be highly soluble or feebly soluble (Larreur-Cayol et al., 2011). In both the cases it will not protect the matrix.

With growing environmental consciousness at all levels of society, the pollution and health hazards, especially associated with the concrete, cement and clay-bricks industries, are coming under intense scrutiny from environmentalists and the governments. Durability and sustainability of Portland cement concrete are other important issues. For making green, durable and sustainable concretes, alternative binders such as geopolymers are being investigated. There are two major environmental benefits of using geopolymer binder over OPC; potential reduced greenhouse gases emissions and utilization of industrial by-products (Neupane, 2016). In principle, geopolymer is a product of alkali activation of any aluminosilicate materials such as fly ash. High early strength and resistance to chemical attack are some of the properties of geopolymer concrete which gave an edge over ordinary Portland cement concrete. Fly ash-based geopolymer can be used as cement to mix with aggregates to form concrete. In this context, considering the low cost, low CO_2 emission and low energy usage in the production of fly ash-based geopolymer, fly ash-based geopolymer cement and concrete are regarded as possible alternative green materials to OPC (Zhuang et al., 2016). These materials are still at the beginning stages of development and hence need further research work in order to become technically and economically viable construction materials.

There is a general consensus about the strength advantages of geopolymer concretes over OPC and there is a widespread debate regarding their durability. Some groups believe that the availability of wide scientific/technical background, together with the already-known OPC durability problems, is sufficient for their commercialization but others consider the durability of geopolymer concretes to be an unproven issue (Arbi et al., 2016). Okoye et al. (2016)

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reported an increase in compressive strength of geopolymer concrete with increase of silica fume. It is also reported that geopolymer in the presence of silica fume is highly resistant to acidic environment (Živica and Križma, 2013) but the role of silica fume is not well understood. From basic concept, durability is defined as the capability of concrete to resist weathering action, chemical attack and abrasion. The preparation and formation, and properties of the fly ash-based geopolymer products depend heavily upon the purity and concentration of alkali solutions and raw materials, chemical and physical characteristics of fly ash, alkali activators and curing conditions. The changes of Si/Al ratios, alkali solutions can lead to the formation of different gels. The gels influence the final structure of geopolymer and control the ionic transport. Alkali solutions influence the hydrolyzation of fly ash and the porosity of geopolymer structure. The porosity influences the migration of alkali from fly ash-based geopolymer into the ion solutions, the moisture and then has an effect on the mechanical strength and durability. Fly ash-based geopolymer with compact and denser structure shows high mechanical strength and good resistance to chloride, sulphate and acid solutions and good efflorescence (Xiao et al., 2016). Incorporation of silica fume into fly ash is expected to improve the mechanical properties of resulting geopolymers by decreasing porosity (Thokchom et al., 2011). No systematic study on the durability of geopolymer concrete in the presence of silica fume is available in the literature. In this paper attempts have been made to investigate the role of silica fume on the durability properties of fly ash based geopolymer concretes in aggressive environment particularly sulphuric acid and sodium chloride solution.

2. Materials and methods

Low calcium fly ash (FA) was used as base material. Fly ash was obtained from National Power station, Dadri, India. Silica fume (SF) was obtained from Ready Mixed Concrete (RMC) industry, Surajpur, Uttar Pradesh, India. The chemical compositions of ordinary Portland cement (OPC), FA and SF used in the experiment are given in Table 1. Coarse aggregates of sizes 0.02 m and 0.01 m with specific gravities 2.5 and 2.4, water absorption of 0.17% and 0.87% and fineness modulus of 2.7 and 2.8 were used. The river sand with specific gravity 2.6 and fineness modulus of 2.1 was also used. The alkali activators used were a mixture of solution of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). To improve workability, naphthalene sulfonate based superplasticizer (SP) was used as chemical admixture. 2% Sulphuric acid (H_2SO_4) and 5% sodium chloride (NaCl) solutions were used for durability experiments.

The detailed mix design of geopolymer concrete (GPC) mixes are given in Table 2. Four concrete mixes were designed. GPC1, GPC2 and GPC3 mixes contain 0, 10 and 20% silica fume along with fly ash.

Table 1
Chemical composition of ordinary Portland cement, Fly ash and Silica fume (Okoye et al., 2016).

Constituents	Chemical composition (%)		
	OPC	FA	SF
Loss on ignition	2.48	3.79	2.10
Silicon Dioxide	19.01	50.70	93.67
Calcium Oxide	66.89	2.38	0.31
Magnesium Oxide	0.81	1.39	0.84
Phosphate (P_20_5)	0.08	–	–
Sodium Oxide	0.09	0.84	0.40
Potassium Oxide	1.17	2.40	1.10
Manganese Oxide	0.19	–	0.84
Aluminium Oxide	4.68	28.80	0.83
Ferric Oxide	3.20	8.80	1.30
Sulphur trioxide	3.0	0.30	0.16

A control Mix40 was cast with OPC for comparison with geopolymer concrete.

Aggregates and binder were first mixed together in dry condition in a mixing pan at room temperature and then the alkali solutions with super plasticizer were mixed with dry materials. After mixing, the concrete mixture was cast in a 0.1 m × 0.1 m x 0.1 m steel mould. The concrete specimens were demoulded after 48 h and cured in oven at 100 °C for 72 h. The specimens were left at room temperature for 28 d before performing durability tests. OPC concrete was cured in water at laboratory temperature for 28 d.

The concrete specimens were immersed in 2% H_2SO_4 and 5% NaCl solutions separately. The effects of these chemicals on GPC1, GPC2, GPC3 and M40 were evaluated through visual observation, changes in weight and percent losses in compressive strength. The period of exposure was 3, 28, 56 and 90 d.

Scanning electron microscopic (SEM) and energy dispersive X-ray (EDX) studies of GPC3 exposed to 2% H_2SO_4 for 90 d were made as this sample was found to have maximum durability.

3. Results and discussions

3.1. Sulphuric acid resistance

3.1.1. Visual appearance

Fig. 1 shows the effect of 2% sulphuric acid solution on GPC3 and M40 concretes for a period of 90 d. The appearance of the specimens showed that GPC3 containing 20% SF did not undergo any deterioration in acid solution nor erosion of surface. M40 concrete showed surface erosion and cutting of edges.

3.1.2. Changes in weight

Percent weight losses of concretes in 2% H_2SO_4 with time are shown in Fig. 2. All the concretes showed weight losses with time of exposure. The overall performance showed that the weight losses of GPC (GPC1, GPC2 and GPC3) were less compared to M40 concrete.

The highest weight loss in 2% H_2SO_4 solution was found for M40 concrete. This was due to chemical reaction between calcium hydroxide/C-S-H gel of M40 and the acid. The chemical reactions caused surface erosion in the concrete as seen visually (Fig. 1b). Conventional OPC concretes are susceptible to acid attack at all the ages of exposure due to the presence of C-S-H gel. In geopolymer concretes, the formation of N-A-S-H and C-A-S-H posed a strong resistance to acid attack. Khatri et al. (1997) reported that the cracking and scaling of OPC concrete are due to acid attack on CH. This increases the porosity, leading to loss of weight. In GPC, FA and SF contain high amount of Al and Si compounds, which react with calcium hydroxide yielding more stable C-A-S-H with a higher filler effect in the concrete pores resulting into lesser weight loss (Aydin et al., 2007). Low weight loss in GPC (on an average the weight loss in GPC3 was lower as compared to GPC1 and GPC2) may be as a result of low permeability of solution and low calcium content as compared to conventional OPC concrete (Pacheco-Torgal et al., 2009).

3.1.3. Changes in compressive strength

The durabilities of GPC containing silica fumes were evaluated by measuring the compressive strength on immersion in 2% H_2SO_4. The variation of compressive strengths of specimens after exposure to 2% H_2SO_4 for different duration are given in Fig. 3 and the variation of percent losses in compressive strengths are shown in Fig. 4.

Fig. 3 shows that compressive strength in the case of M40 concrete decreased continuously with exposure time. In the case of GPC1 without silica fume, the compressive strength also decreased with exposure time but the decrease was lower as compared to

Table 2
Mix proportion of geopolymer concretes.

MIX NO	Quantity of ingredients (Kg/m^3)										
	Coarse Aggregate		Fine Sand	FA	SF	OPC	Na_2SiO_3	NaOH (14M)	SP	Alkali/FA	Water/Solid
	20 mm	10 mm									
GPC1	862	431	554	400		0	113	45	4.0	0.4	0.2
GPC2	862	431	554	360	40	0	113	45	4.0	0.4	0.2
GPC3	862	431	554	320	80	0	113	45	4.0	0.4	0.2
M40	862	431	554	0	0	400	0	0	4.0	0	0.3

(a) (b)

Fig. 1. Visual appearance of four blocks of each (a) GPC3 and (b) M40 concretes after immersing in 2% H_2SO_4 solution for a period of 90 d.

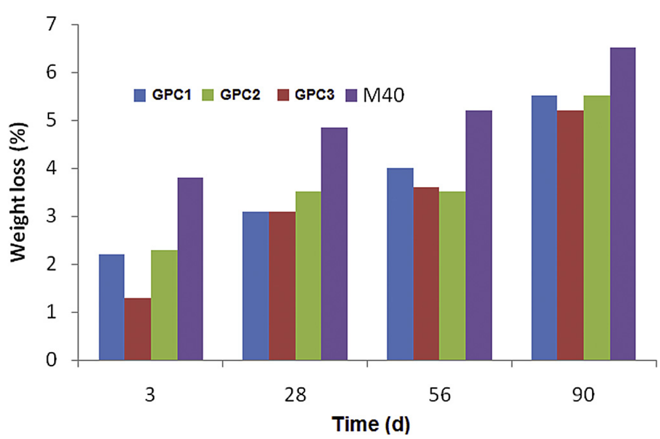


Fig. 2. Variation of percent weight losses in GPC (GPC1, GPC2 and GPC3) and M40 concretes in 2% Sulphuric acid solution as a function of exposure time.

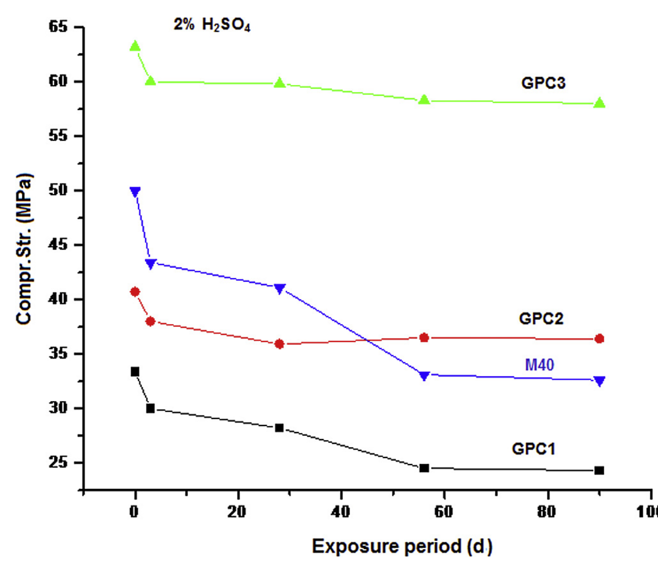


Fig. 3. Variation of compressive strengths of GPC and M40 exposed to 2% H_2SO_4 at different exposure time.

M40 concrete. Further with the addition of silica fume particularly in presence of 20% silica fume (GPC3), there was a very low decrease in compressive strength with exposure time.

In order to have direct information about the loss in strength relating to deterioration, the percent loss in compressive strength with exposure time in 2% H_2SO_4 was calculated and given in Fig. 4. There is a rapid increase in the percent loss in compressive strength with exposure time in the case of M40 concrete. In the case of GPC1, percent loss in the compressive strength also increased with exposure time but much lower than that of M40. The percent loss in the compressive strength was minimum in the case of GPC3 containing 20% silica fume and was almost constant till 90 d. The results showed that GPC containing silica fume performs better than OPC concrete when exposed to acid environment.

Since GPC3 showed minimum loss in compressive strength on exposure to 2% H_2SO_4 for 90 d. SEM and EDX were recorded (Fig. 5). The results did not show any sign of deterioration in the sample.

The lifetime of Portland cement concrete can be severely shortened in the acidic environment because of reaction of calcium compounds present in the concrete. Contrary to this, the end product of geopolymerisation is N-A-S-H which shows high resistance to acid attack. The loss in strength of control concrete (M40) was as a result of formation of ettringite and gypsum in the pores of the specimen. The loss in strength of different GPC may be as a result of pore size distribution and varying dissolution rates of source materials (Okoye et al., 2016). The formation of micro pores on the surface of concretes due to poor compaction might have resulted in the loss of strength. Micro pores might have increased the permeability of the solution into the concretes, causing attack

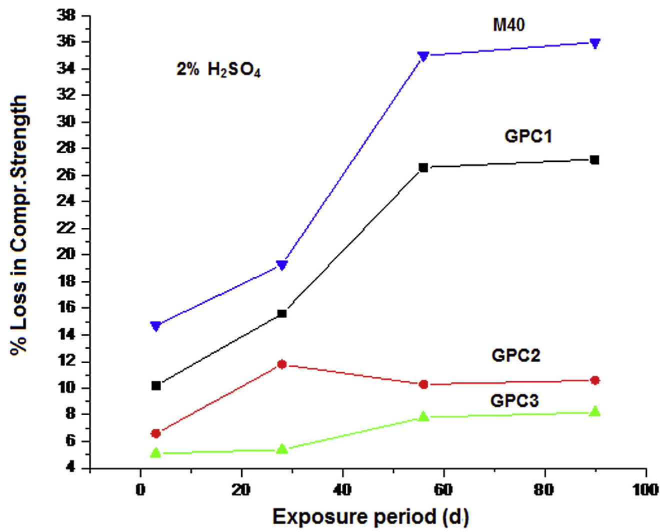


Fig. 4. Variation of percent loss in compressive strength in GPC and M40 exposed to 2% H_2SO_4 at different exposure time.

and subsequent decrease in strength. For fly ash-based geopolymer concrete, the acid attack may be associated with the depolymerization of aluminosilicate network structure and the liberation of silicic acid ($Si(OH)_4$). When immersed in a strong acid solution, Na^+ and K^+ ions from fly ash-based geopolymer could be substituted by H^+ or H_3O^+, breaking −Si−O−Al− and −Si−O−Si− bonds, and releasing silicic acid (Zhuang et al., 2016). Ariffin et al. (2013) reported 35% strength loss for blended FA geopolymer concrete after 18 months exposure to H_2SO_4 solution, while OPC concrete lost 68% during the same period. Duan et al. (2015), reported strength loss of 10.5% and 22.2% in 28 and 60 d when geopolymer concrete was exposed to 2% HCl solution. OPC concrete lost 34.4% and 57.8% during the same period. It is found that incorporation of silica fume in FA based GPC enhanced its durability properties and protected concrete structures from chemical attack. High mechanical strength and durability performance of GPC containing silica fume could be attributed due to increased geopolymerisation, reduction in pore size and permeability of acid solution in the concrete.

The better performance of geopolymeric materials than that of Portland cement concrete in acidic environment might be attributed to the lower calcium content in the fly ash as a main possible factor since geopolymer concrete does not rely on lime like Portland cement concrete. Geopolymer concrete does not have transition zone and hence does not allow the ingress of sulphuric acid. These factors are also responsible for higher durability of geopolymer concretes.

3.2. Chloride resistance

3.2.1. Visual appearance

The effect of chloride on the physical structure of GPC3 containing 20% SF was evaluated by visual observation after 90 d of exposure in 5% NaCl solution (Fig. 6). There was no deterioration or erosion of surface.

3.2.2. Weight loss of specimens in presence of 5% NaCl solution

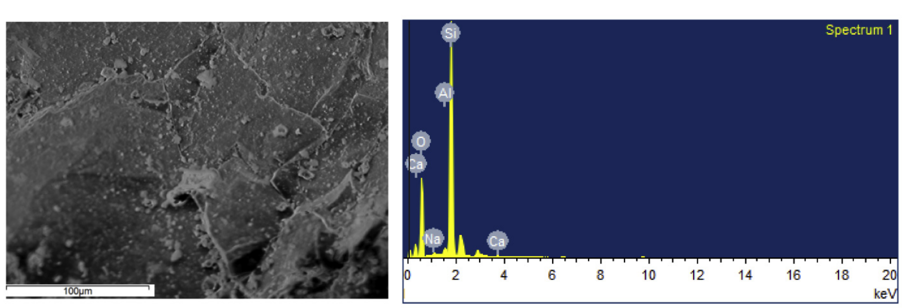
Fig. 7 shows percent weight loss changes in GPC and M40 when exposed to 5% NaCl solution for different periods.

The results showed that there was a slight weight loss in all the GPC samples during the period of exposure to NaCl environment. The weight losses in GPC were less as compared to M40 indicating that GPC were more resistant to chloride attack. The physical appearance of GPC was not altered after 90 d of exposure. The high decrease in weight of M40 could be attributed to depletion of C-S-H in chloride medium which caused deterioration of concrete samples and subsequent loss of weight. The slight reduction in weight of GPC may be as a result of formation of high resistant N-A-S-H. The results have shown that GPC particularly GPC3 containing 20% SF in NaCl solution deteriorates very little or practically does not deteriorate. This indicates that SF blocks the pores and makes the concrete compact.

3.2.3. Compressive strength of specimens exposed to 5% NaCl solution

The variations of compressive strengths of specimens after exposure to 5% NaCl solution for different duration are given in

Fig. 6. Visual observation of GPC3 exposed to 5% NaCl solution for 90 d.



(a) (b)

Fig. 5. (a) SEM picture and (b) EDX of GPC3 in 2% H_2SO_4 for 90 d.

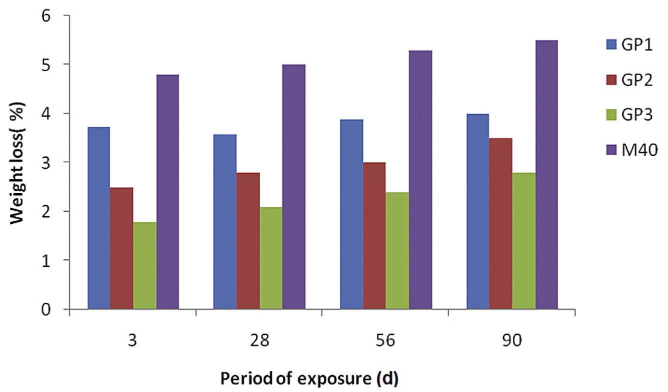


Fig. 7. Changes in weight of GPC and M40 in 5% NaCl solution exposed for different periods.

Fig. 8. The variations of percent losses in compressive strengths are given in Fig. 9.

The results showed that there was a continuous reduction in strength of control sample (M40) when exposed to chloride solution. There was a slow decrease in compressive strength in the case of GPC1 and GPC2 and practically no decrease in GPC3. The percent loss in compressive strength of M40 (control) increased continuously with exposure time whereas there was a slow increase in the percent loss of compressive strength with exposure time in GPC1 and GPC2. Practically there was no loss in compressive strength in GPC3 containing 20% silica fume. Resistance to chloride is one of the main areas of durability of cement and concrete. Chloride penetration promotes the corrosion of the embedded steel bars when steel bars are used as reinforcements for geopolymer concrete. Chloride penetrates into fly ash-based geopolymer occurs through capillary absorption, hydrostatic pressure and diffusion of ions. The relatively high concentration of NaOH enabled the leaching of more Si^{4+} and Al^{3+} from fly ash and produced a better degree of polycondensation and resulted in the decrease of porosity of fly ash based geopolymer. The porosity was further decreased in the presence of 20% silica fume, which decreased chloride penetration. As a result, the geopolymer concrete became resistant to chloride attack (Zhuang et al., 2016).

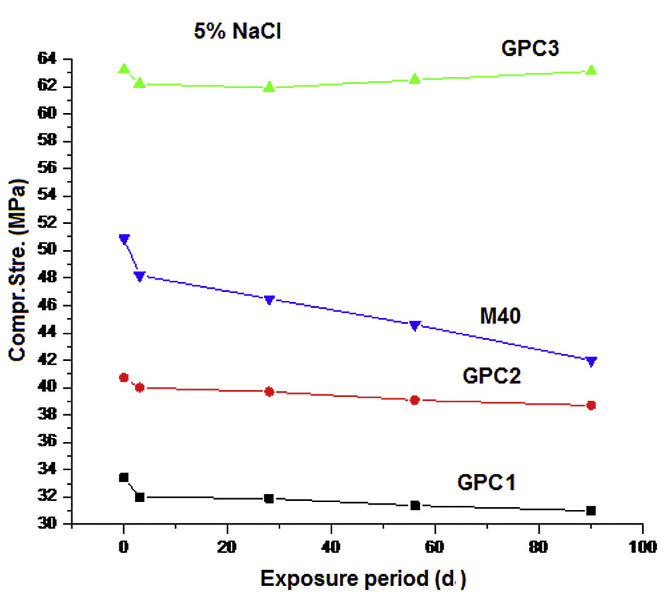


Fig. 8. Variation of compressive strength of GPC1, GPC2, GPC3 and M40 with exposure time in presence of 5% NaCl solution.

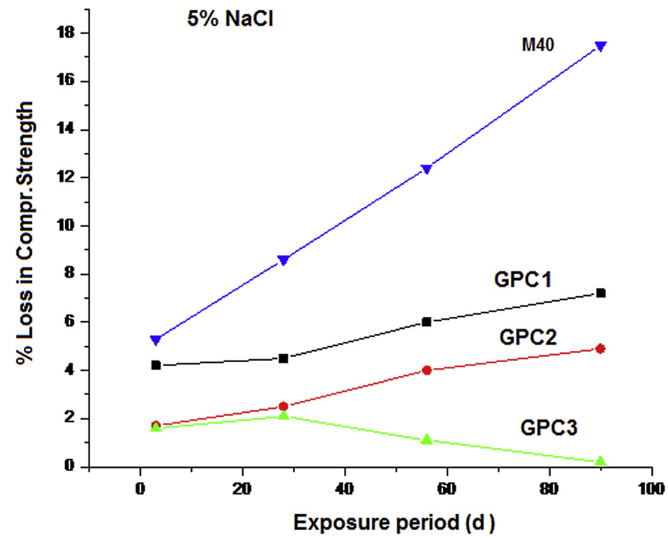


Fig. 9. Variation of percent loss in compressive strength of GPC1, GPC2, GPC3 and M40 with exposure time in presence of 5% NaCl solution.

4. Economic benefits of geopolymer concrete

Fly ash-based geopolymer concrete offers several economic benefits over Portland cement concrete. The cost of one tonne (t) of fly ash is only a small fraction, if not free in some parts of the world, as compared the cost of one tonne (t) of Portland cement. After allowing for the cost of activator liquids needed to make the geopolymer concrete, fly ash-based geopolymer concrete will be cheaper than that of Portland cement concrete (Lloyd and Rangan, 2010). As per Indian Standard (IS) 456: 2000, the cost of one cubic meter of Portland cement concrete is about 60 USD whereas it is 45 USD for one cubic meter of geopolymer concrete. Thus geopolymer concrete is about 25% cheaper. This will vary from country to country depending on the availability and price of raw materials. In addition, the appropriate usage of one tonne (t) of fly ash earns approximately one carbon-credit that has a significant redemption value. One tonne (t) fly ash can be utilized to manufacture approximately 2.5 cubic meters of geopolymer concrete. This carbon credit significantly adds to the economy offered by the geopolymer concrete (Hardjito and Rangan, 2005). The low drying shrinkage, the low creep, the excellent resistance to sulfate attack, good acid resistance, and excellent fire resistance offered by geopolymer concrete may yield additional economic benefits when it is utilized in infrastructure applications.

5. Concluding remarks

In this study durability properties of fly ash based geopolymer concretes in the presence and absence of silica fume have been studied in the corrosive atmosphere of 2% H_2SO_4 and 5% NaCl solutions. Results were compared with that of the control. Visual observations revealed that there was surface erosion and cutting of edges in the case of OPC concrete but no erosion in the case of geopolymer concrete containing 20% silica fume when exposed to 2% H_2SO_4 and 5% NaCl solution for 90 d. 2% H_2SO_4 was found to be more corrosive as compared to 5% NaCl solution. Compressive strength losses in the case of geopolymer concrete containing 20% silica fume were negligible in the presence of 2% H_2SO_4 and 5% NaCl solutions. Geopolymer concrete in presence of 20% silica fume possessed excellent long term durability properties capable of resisting chemical attack. In order to have more informations about durability, geopolymer concretes in the presence of different amounts of silica fume be made and treated with different concentrations of H_2SO_4 and NaCl.

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