

A STUDY ON PERFORMANCE OF FLY ASH BASED GEOPOLYMER CONCRETE IN CHEMICAL ATMOSPHERE

¹G.S.V.Brahammaji and ²P.Venkata Muthyalu

¹P.G Student, KITS, Divili

²Assistant Professor & HOD, Pragati Engineering College, A.P, India

ABSTRACT

Geopolymer concrete results from the reaction of a source material that is rich in silica and alumina with alkaline liquid. The term geopolymer was introduced by Davidovits, geopolymers are members of the family of inorganic polymers. Geopolymer binders have been reported as being acid resistant and thus are promising and alternative binders for sewer pipe manufacture. This paper presents experimental data on the Behavior of fly ash based geopolymer concretes exposed chemical solutions for up to 4 weeks. A class F fly ash based geopolymer concrete was initially cured for 24 hours at 60°C. And also the obtained results are compared with the conventional concretes exposed to 5% acid solutions for up to 4 weeks. The compressive strength of geopolymer concretes and conventional concretes of 150-mm cubes at an age of 28 days are 32MPa and 48.5MPa. Initially concrete cubes were cured for a period of 28 days and later cubes were immersed in chemical solutions, After immersion in chemical solutions, samples were tested at 7, 14 and 28 days. The mass loss, compressive strength reductions were determined. In this experimental work 3 type of chemical solutions are used that are HCl, H₂SO₄ and MgSO₄. The results confirmed that Geopolymer concrete is highly resistant to acid in terms of a very low mass loss and compressive strength loss when compared to conventional concrete.

I. GENERAL

Concrete usage around the world is second only to water. Ordinary Portland cement (OPC) is conventionally used as the primary binder to produce concrete. The environmental issues associated with the production of OPC are well known. The amount of the carbon dioxide released during the manufacture of OPC due to the calcination of limestone and combustion of fossil fuel is in the order of one ton for every ton of OPC produced. In addition, the extent of energy required to produce OPC is only next to steel and aluminum.

On the other hand, the abundant availability of fly ash worldwide creates opportunity to utilize this by-product of burning coal, as a substitute for OPC to manufacture concrete. When used as a partial replacement of OPC, in the presence of water and in ambient temperature, fly ash reacts with the calcium hydroxide during the hydration process of OPC to form the calcium silicate hydrate (C-S-H) gel. The development and application of high volume fly ash concrete, which enabled the replacement of OPC up to 60% by mass (Malhotra 2002; Malhotra and Mehta 2002), is a significant development. In 1978, Davidovits (1999) proposed that binders could be produced by a polymeric reaction of alkaline liquids with the silicon and the aluminum in source materials of geological origin or by-product materials such as fly ash and rice husk ash. He termed these binders as geopolymers. Palomo et al (1999) suggested that pozzolans such as blast furnace slag might be activated using alkaline liquids to form a binder and hence totally replace the use of OPC in concrete. In this scheme, the main contents to be activated are silicon and calcium in the blast furnace slag. The main binder produced is a C-S-H gel, as the result of the hydration process.

In spite of a long-term recognition of the problem of sulphuric acid corrosion in concrete sewer pipes, this issue has not been satisfactorily resolved. A research looked at ways of enhancing the acid resistance of Portland Cement (PC) based concretes, using the partial replacement of Portland cement by supplementary materials, the use of epoxy modified binders, and the use of limestone as a

sacrificial aggregate [Song et al 2003]. The acid attack in terms of mass loss was reduced. However, even the improved concretes lost significant mass with immersion time. Sulphuric acid resistant binders are still required to enhance the long-term performance of concrete in sulphuric acid corrosion environments. Sulphur concrete is sulphuric acid resistant. However, weighing the advantages and limitations of sulphur concrete based on the available published data, Malhotra [1988] emphasised that the indiscriminate use of sulphur as a binder for concrete cannot be recommended.

Geopolymer binders might be a promising alternative in the development of acid resistant concrete. Since Geopolymers are a novel binder that relies on alumina-silicate rather than calcium silicate hydrate bonds for structural integrity, they have been reported as being acid resistant.

In 2001, when this research began, several publications were available describing geopolymer pastes and geopolymer coating materials (Davidovits 1991; Davidovits 1994; Davidovits et al. 1994; Balaguru, et al. 1997; van Jaarsveld, et al. 1997; Balaguru 1998; van Jaarsveld et al. 1998; Davidovits 1999; Kurtz et al. 1999; Palomo et al. 1999; Barbosa et al. 2000). However, very little was available in the published literature regarding the use of geo polymer technology to make low calcium (ASTM Class F) fly ash-based geopolymer concrete.

II. REVIEW LITERATURE

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 'tradeable emissions' refers to the economic mechanisms that are expected to help the countries worldwide to meet the emission reduction targets established by the 1997 Kyoto Protocol. Speculation has arisen that one ton of emissions can have a trading value about US\$10 (Malhotra 1999; Malhotra 2004).

The climate change is attributed to not only the global warming, but also to the paradoxical global dimming due to the pollution in the atmosphere. Global dimming is associated with the reduction of the amount of sunlight reaching the earth due to pollution particles in the air blocking the sunlight. With the effort to reduce the air pollution that has been taken into implementation, the effect of global dimming may be reduced; however it will increase the effect of global warming (Fortune 2005).

From this point of view, the global warming phenomenon should be considered more seriously, and any action to reduce the effect should be given more attention and effort.

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).

The contribution of Portland cement production worldwide to the greenhouse gas emission is estimated to be about 1.35 billion tons annually or about 7% of the total greenhouse gas emissions to the earth's atmosphere (Malhotra 2002). Cement is also among the most energy-intensive construction materials, after aluminium and steel.

Furthermore, it has been reported that the durability of ordinary Portland cement (OPC) concrete is under examination, as many concrete structures, especially those built in corrosive environments, start to deteriorate after 20 to 30 years, even though they have been designed for more than 50 years of service life (Mehta and Burrows 2001).

The concrete industry has recognized these issues. For example, the U.S. Concrete Industry has developed plans to address these issues in 'Vision 2030: A Vision for the U.S. Concrete Industry'. The document states that *'concrete technologists are faced with the challenge of leading future development in a way that protects environmental quality while projecting concrete as a construction material of choice. Public concern will be responsibly addressed regarding climate change resulting from the increased concentration of global warming gases.* In this document, strategies to retain concrete as a construction material of choice for infrastructure development, and at the same time to make it an environmentally friendly material for the future have been outlined (Mehta 2001; Plenge 2001).

In order to produce environmentally friendly concrete, Mehta (2002) suggested the use of fewer natural resources, less energy, and minimize carbon dioxide emissions.

He categorized these short-term efforts as *'industrial ecology'*. The long-term goal of reducing the impact of unwanted by-products of industry can be attained by lowering the rate of material

consumption. Likewise, McCaffrey (2002) suggested that the amount of carbon dioxide (CO₂) emissions by the cement industries can be reduced by decreasing the amount of calcined material in cement, by decreasing the amount of cement in concrete, and by decreasing the number of buildings using cement.

Fly Ash

According to the American Concrete Institute (ACI) Committee 116R, fly ash is defined as '*the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gases from the combustion zone to the particle removal system*' (ACI Committee 232 2004). Fly ash is removed from the combustion gases by the dust collection system, either mechanically or by using electrostatic precipitators, before they are discharged to the atmosphere. Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1 μ to no more than 150 μm.

The types and relative amounts of incombustible matter in the coal determine the chemical composition of fly ash. The chemical composition is mainly composed of the oxides of silicon (SiO₂), aluminium (Al₂O₃), iron (Fe₂O₃), and calcium (CaO), whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount. The major influence on the fly ash chemical composition comes from the type of coal. The combustion of sub-bituminous coal contains more calcium and less iron than fly ash from bituminous coal. The physical and chemical characteristics depend on the combustion methods, coal source and particle shape.

The chemical compositions of various fly ashes show a wide range, indicating that there is a wide variation in the coal used in power plants all over the world (Malhotra and Ramezani-pour 1994).

Fly ash that results from burning sub-bituminous coals is referred to as ASTM Class C fly ash or high-calcium fly ash, as it typically contains more than 20 percent of CaO. On the other hand, fly ash from the bituminous and anthracite coals is referred to as ASTM Class F fly ash or low-calcium fly ash. It consists of mainly an aluminosilicate glass, and has less than 10 percent of CaO. The colour of fly ash can be tan to dark grey, depending upon the chemical and mineral constituents (Malhotra and Ramezani-pour 1994; ACAA 2003). The typical fly ash produced from Australian power stations is light to mid-grey in colour, similar to the colour of cement powder. The majority of Australian fly ash falls in the category of ASTM Class F low calcium fly ash, and contains 80 to 85% of silica and alumina (Heidrich 2002).

Aside from the chemical composition, the other characteristics of fly ash that are generally considered are loss on ignition (LOI), fineness and uniformity. LOI is a measurement of unburnt carbon remaining in the ash. Fineness of fly ash mostly depends on the operating conditions of coal crushers and the grinding process of the coal itself. Finer gradation generally results in a more reactive ash and contains less carbon.

In 2001, the annual production of fly ash in the USA was about 68 million tons. Only 32 percent of this was used in various applications, such as in concrete, structural fills, waste stabilization/solidification etc. (ACAA 2003). Ash production in Australia in 2000 was approximated at 12 million tons, with some 5.5 million tons having been utilised (Heidrich 2002). Worldwide, the estimated annual production of coal ash in 1998 was more than 390 million tons. The main contributors for this amount were China and India. Only about 14 percent of this fly ash was utilized, while the rest was disposed in landfills (Malhotra 1999). By the year 2010, the amount of fly ash produced worldwide is estimated to be about 780 million tons annually (Malhotra 2002). The utilization of fly ash, especially in concrete production, has significant environmental benefits, viz, improved concrete durability, reduced use of energy, diminished greenhouse gas production, reduced amount of fly ash that must be disposed in landfills, and saving of the other natural resources and materials (ACAA 2003)

Geopolymers

In 1978, Davidovits proposed that an alkaline liquid could be used to react with the silicon (Si) and the aluminum (Al) in a source material of geological origin or in byproduct materials such as fly ash and rice husk ash to produce binders. Because the chemical reaction that takes place in this case is a polymerization process, he coined the term 'Geopolymer' to represent these binders.

Davidovits (1999) calcined kaolin clay for 6 hours at 750°C. He termed this metakaolin as KANDOXI (KAolinite, Nacrite, DickiteOXIde), and used it to make geopolymers. For the purpose of making geopolymer concrete, he suggested that the molar ratio of Si-to-Al of the material should be about 2.0 (Table 2.1).

On the nature of the source material, it was stated that the calcined source materials, such as fly ash, slag, calcined kaolin, demonstrated a higher final compressive strength when compared to those made using non-calcined materials, for instance kaolin clay, mine tailings, and naturally occurring minerals (Barbosa et al. 2000). However, Xu and van Deventer (2002) found that using a combination of calcined (e.g. fly ash) and non-calcined material (e.g. kaolinite or kaolin clay and albite) resulted in significant improvement in compressive strength and reduction in reaction time.

Natural Al-Si minerals have shown the potential to be the source materials for geopolymerisation, although quantitative prediction on the suitability of the specific mineral as the source material is still not available, due to the complexity of the reaction mechanisms involved (Xu and van Deventer 2000). Among the by-product materials, only fly ash and slag have been proved to be the potential source materials for making geopolymers. Fly ash is considered to be advantageous due to its high reactivity that comes from its finer particle size than slag. Moreover, low-calcium fly ash is more desirable than slag for geopolymer feedstock material.

The suitability of various types of fly ash to be geopolymer source material has been studied by Fernández-Jiménez and Palomo (2003). These researchers claimed that to produce optimal binding properties, the low-calcium fly ash should have the percentage of unburned material less than 5%, Fe₂O₃ content should not exceed 10%, and low CaO content, the content of reactive silica should be between 40-50%, and 80-90% of particles should be smaller than 45 µm. On the contrary, van Jaarsveld et al (2003) found that fly ash with higher amount of CaO produced higher compressive strength, due to the formation of calcium-aluminate-hydrate and other calcium compounds, especially in the early ages. The other characteristics that influenced the suitability of fly ash to be a source material for geopolymers are the particle size, amorphous content, as well as morphology and the origin of fly ash.

Alkaline Liquids

The most common alkaline liquid used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate (Davidovits 1999; Palomo et al. 1999; Barbosa et al. 2000; Xu and van Deventer 2000; Swanepoel and Strydom 2002; Xu and van Deventer 2002).

Palomo et al (1999) concluded that the type of alkaline liquid plays an important role in the polymerisation process. Reactions occur at a high rate when the alkaline liquid contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. Xu and van Deventer (2000) confirmed that the addition of sodium silicate solution to the sodium hydroxide solution as the alkaline liquid enhanced the reaction between the source material and the solution. Furthermore, after a study of the geopolymerisation of sixteen natural Al-Si minerals, they found that generally the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution.

Mixture Proportions

The primary difference between geopolymer concrete and Portland cement concrete is the binder. The silicon and aluminium oxides in the low-calcium fly ash reacts with the alkaline liquid to form the geopolymer paste that binds the loose coarse aggregates, fine aggregates, and other un-reacted materials together to form the geopolymer concrete.

As in the case of Portland cement concrete, the coarse and fine aggregates occupy about 75 to 80% of the mass of geopolymer concrete. This component of geopolymer concrete mixtures can be designed using the tools currently available for Portland cement concrete.

The compressive strength and the workability of geopolymer concrete are influenced by the proportions and properties of the constituent materials that make the geopolymer paste.

Materials

Fly Ash

In the present experimental work, low calcium, Class F dry fly ash obtained from the Thermal Power Plant , IBRAHIMPATNAM, was used as the base material.

Alkaline Liquid

A combination of sodium silicate solution and sodium hydroxide solution was chosen as the alkaline liquid. Sodium-based solutions were chosen because they were cheaper than Potassium-based solutions.

The sodium hydroxide (NaOH) solution was prepared by dissolving either the flakes or the pellets in water. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, M. For instance, NaOH solution with a concentration of 8M consisted of $8 \times 40 = 320$ grams of NaOH solids (in flake or pellet form) per litre of the solution, where 40 is the molecular weight of NaOH. The mass of NaOH solids was measured as 262 grams per kg of NaOH solution of 8M concentration

The chemical composition of the sodium silicate solution was $\text{Na}_2\text{O}=14.7\%$, $\text{SiO}_2=29.4\%$, and water 55.9% by mass.

III. EXPERIMENTAL WORK

The aggregates were prepared in saturated-surface-dry condition.



Fig:1 Fly-Ash



Fig:2 All The Materials Placed For Mixing



Fig:3 Sodium-silicate and sodium hydroxide solution



Fig:4 Concrete Before Adding Solution



Fig:5 Immersion of concrete cubes



Fig:6.chemical solutions (HCl,H₂SO₄ and MgSO₄)



Fig:7 Concrete cubes after acid immersion in H₂SO₄

Fig:8 Concrete cubes after immersion in MgSO₄

The solids constituents of the fly ash-based geopolymer concrete, i.e. the aggregates and the fly ash, were dry mixed in the pan mixer for about three minutes. The liquid part of the mixture, i.e. the sodium silicate solution, the sodium hydroxide solution, added water (if any), and the super plasticiser (if any), were pre mixed then added to the solids . The wet mixing usually continued for another four minutes.

The fresh fly ash-based geopolymer concrete was dark in colour and shiny in appearance . The mixtures were usually cohesive.

The fresh concrete could be handled up to 120 minutes without any sign of setting and without any degradation in the compressive strength. The fresh concrete was cast and compacted by the usual methods used in the case of Portland cement concrete (Hardjito and Rangan, 2005; Wallah and Rangan, 2006; Sumajouw and Rangan, 2006).

Although low-calcium fly ash-based geopolymer concrete can be cured in ambient conditions, heatcuring is generally recommended. Heat-curing substantially assists the chemical reaction that occurs in the geopolymer paste. Both curing time and curing temperature influence the compressive strength of geopolymer concrete.

Table: 1 Residual compressive strength on acid immersion.

S.No	Type of concrete	Compressive strength at 28days (Before acid immersion) (N/mm ²)	Compressive strength After 7 days of acid immersion (N/mm ²)			Compressive strength After 14 days of acid immersion (N/mm ²)			Compressive strength After 28 days of acid immersion (N/mm ²)		
			Type of Acid			Type of Acid			Type of Acid		
			HCl	H ₂ SO ₄	MgSO ₄	HCl	H ₂ SO ₄	MgSO ₄	HCl	H ₂ SO ₄	MgSO ₄
1	Conventional concrete(M30)	49.83	44.34	35	45	42.35	29	44	40.86	21	42
2	Geopolymer concrete	32	29.44	27.36	28.8	28.8	25.69	27.52	27.5	23.2	26.4

Table: 2 Percentage loss of compressive strength on acid immersion.

S.No	Type of concrete	% loss of Compressive strength After 7 days of acid immersion(N/mm ²)			% loss of Compressive strength After 14 days of acid immersion (N/mm ²)			% loss of Compressive strength After 28 days of acid immersion (N/mm ²)		
		Type of Acid			Type of Acid			Type of Acid		
		Hcl	H ₂ SO ₄	MgSO ₄	Hcl	H ₂ SO ₄	MgSO ₄	Hcl	H ₂ SO ₄	MgSO ₄
1	Conventional concrete(M30)	11	29.76	9.61	15	41.80	11.69	18	57.85	15.65
2	Geopolymer concrete	8	14.5	9	10	19.7	14	14.06	27.5	17.5

Durability Studies**Table: 3** Conventional concrete

S.No	Type of Acid	Weight of concrete cubes after 28 days of casting and before acid immersion in days for (Kg)			Weight of concrete cubes after acid immersion in days (Kg)		
		7	14	28	7	14	28
1	Hcl	8.78	8.80	8.76	8.58	8.53	8.43
2	H ₂ SO ₄	8.79	8.78	8.7	8.30	8.20	8.0
3	MgSO ₄	8.78	8.79	8.8	8.60	8.60	8.56

Table: 4 Geopolymer concrete

S.No	Type of Acid	Weight of concrete cubes after 28 days of casting and before acid immersion in days for (Kg)			Weight of concrete cubes after acid immersion in days (Kg)		
		7	14	28	7	14	28
1	Hcl	7.84	7.85	7.83	7.8	7.79	7.76
2	H ₂ SO ₄	7.95	7.78	7.82	7.87	7.64	7.65
3	MgSO ₄	7.88	7.9	7.8	7.85	7.86	7.74

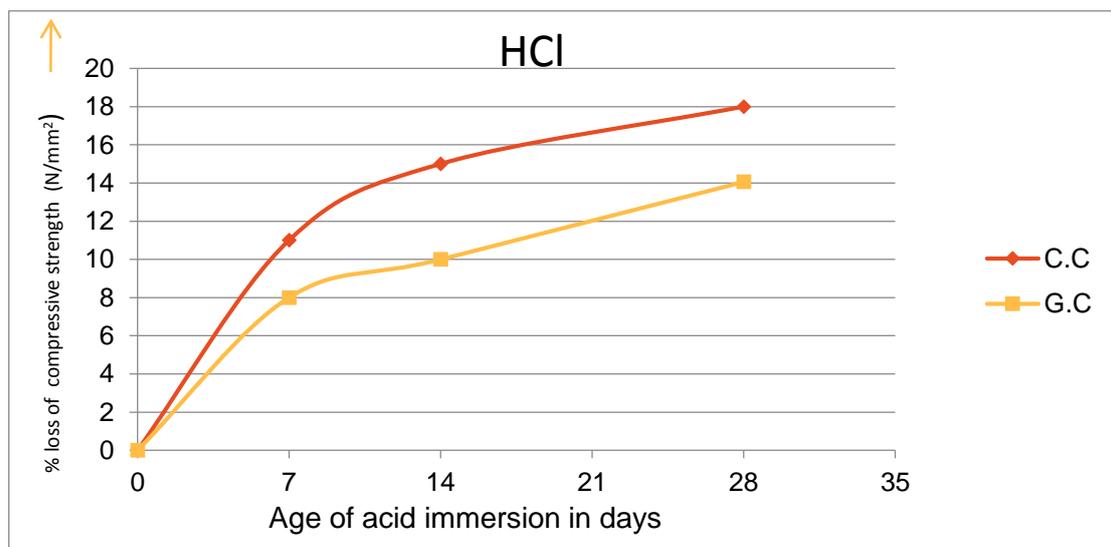
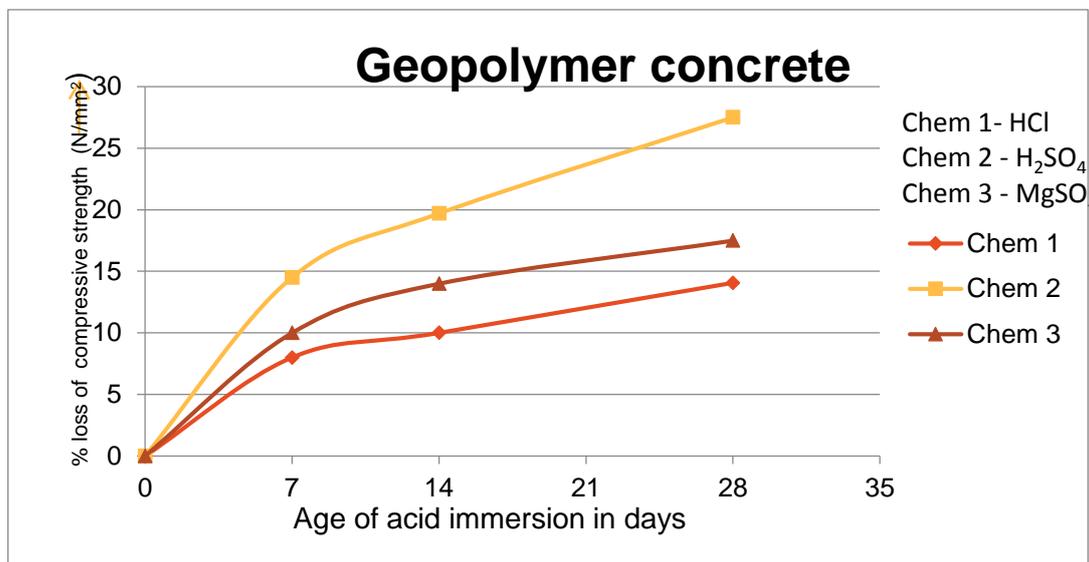
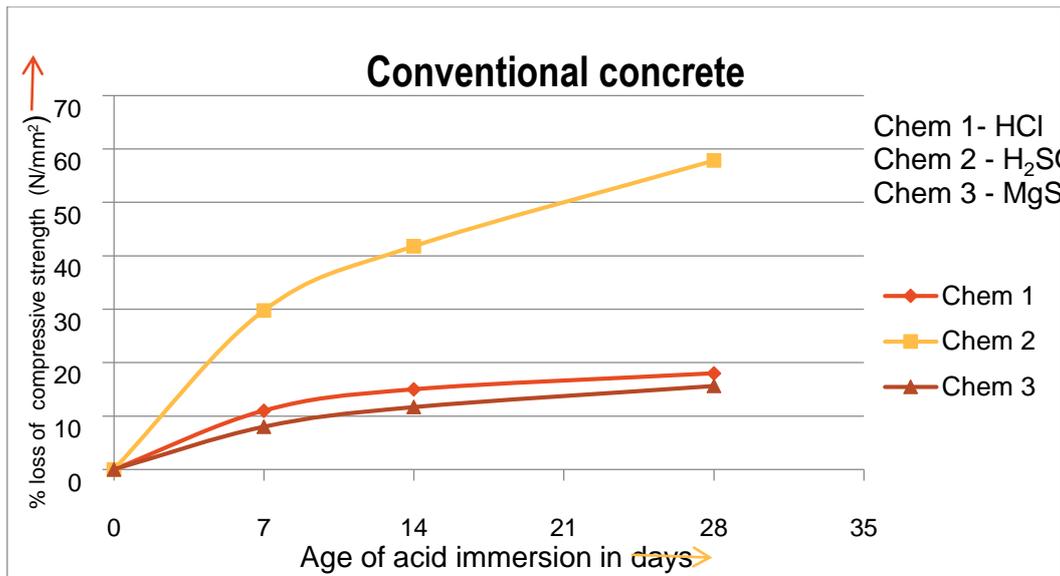
Percentage weight loss on acid immersion.**Table: 5** Conventional concrete

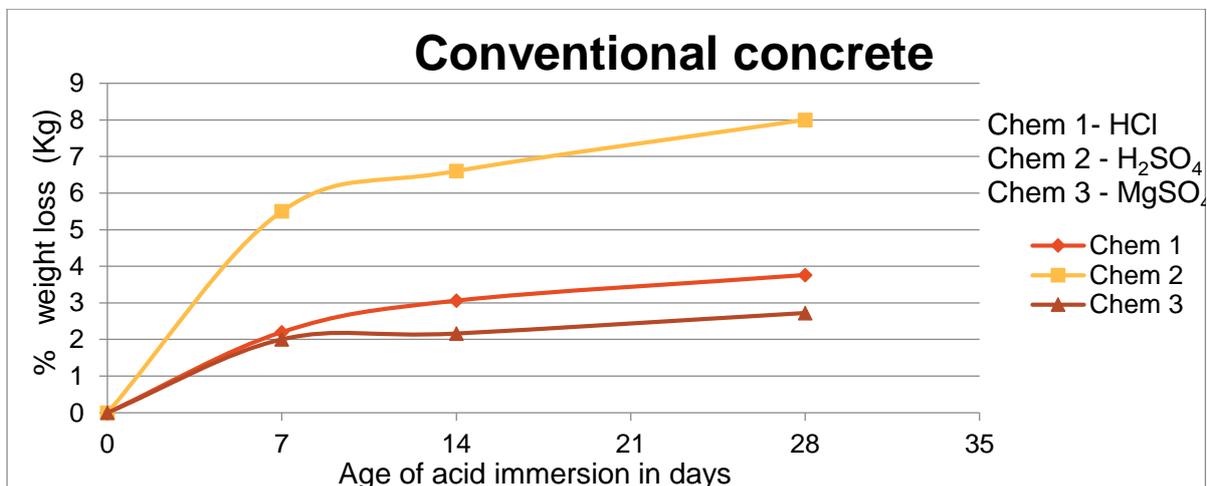
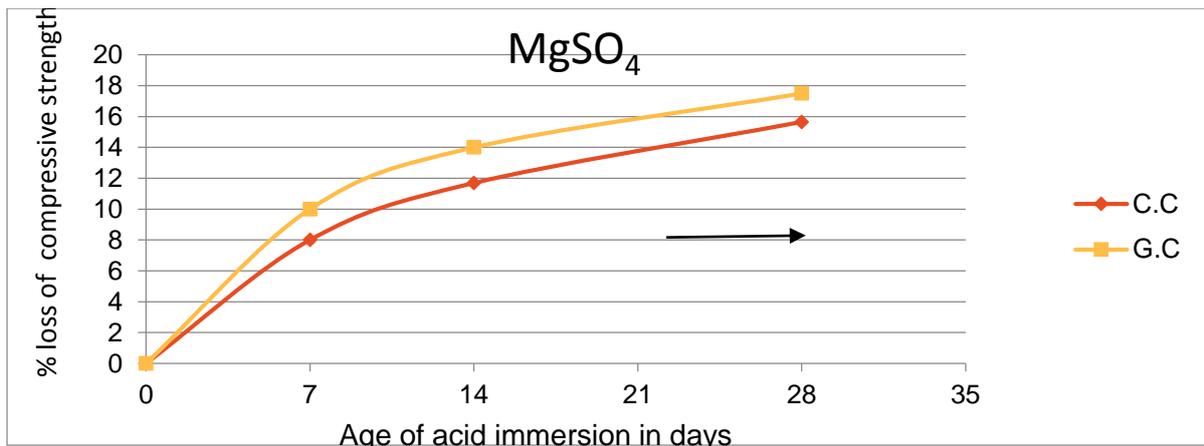
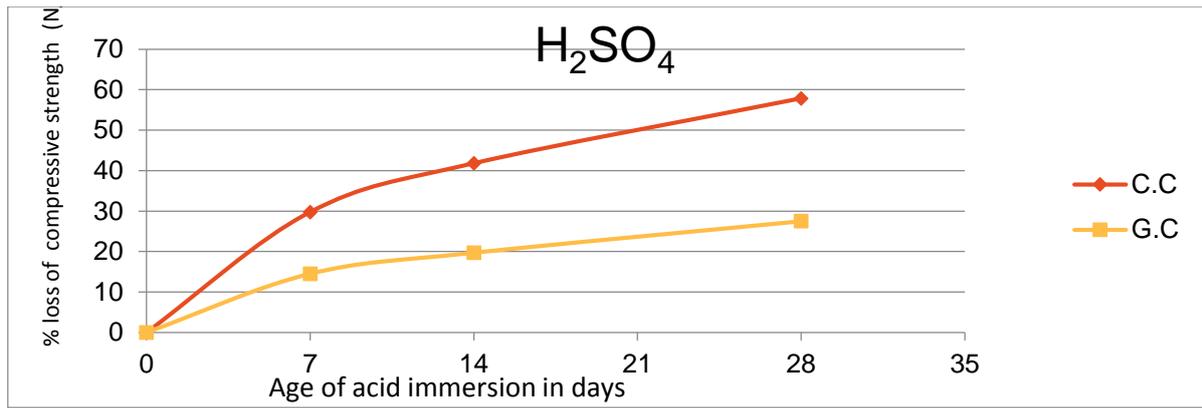
S.No	Type of Acid	% Weight loss of concrete cubes after acid immersion		
		Age of acid immersion in days		
		7	14	28
1	Hcl	2.2%	3.06%	3.76%
2	H ₂ SO ₄	5.5%	6.6%	8%
3	MgSO ₄	2.0%	2.16%	2.72%

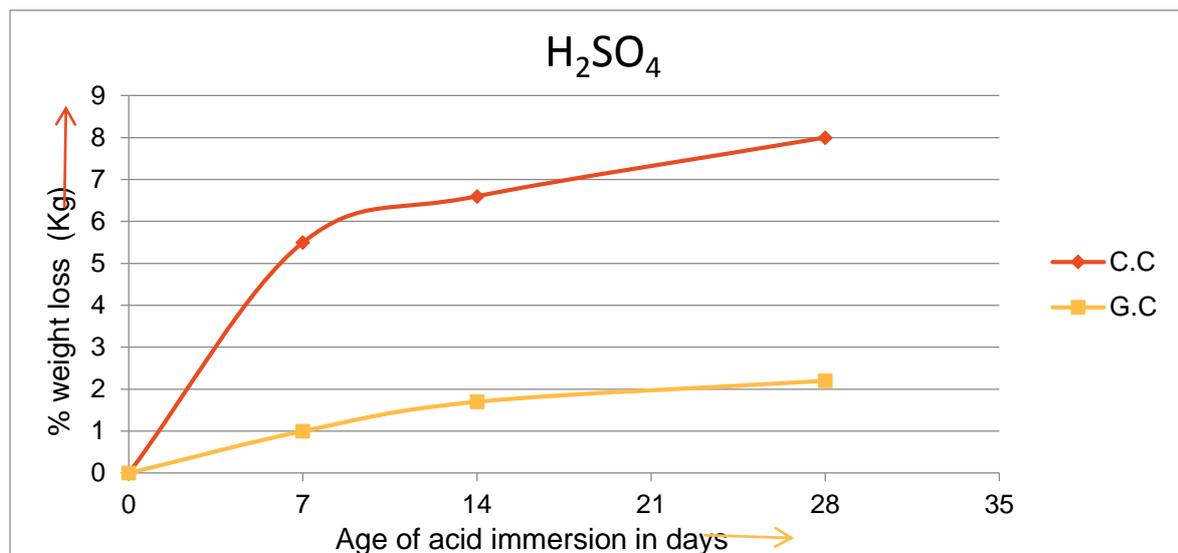
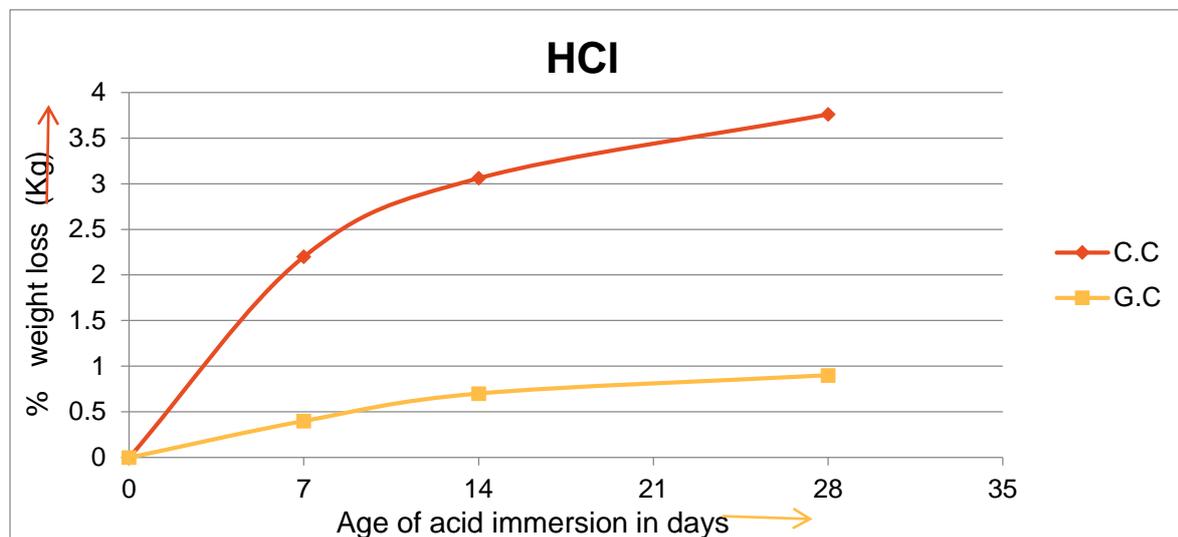
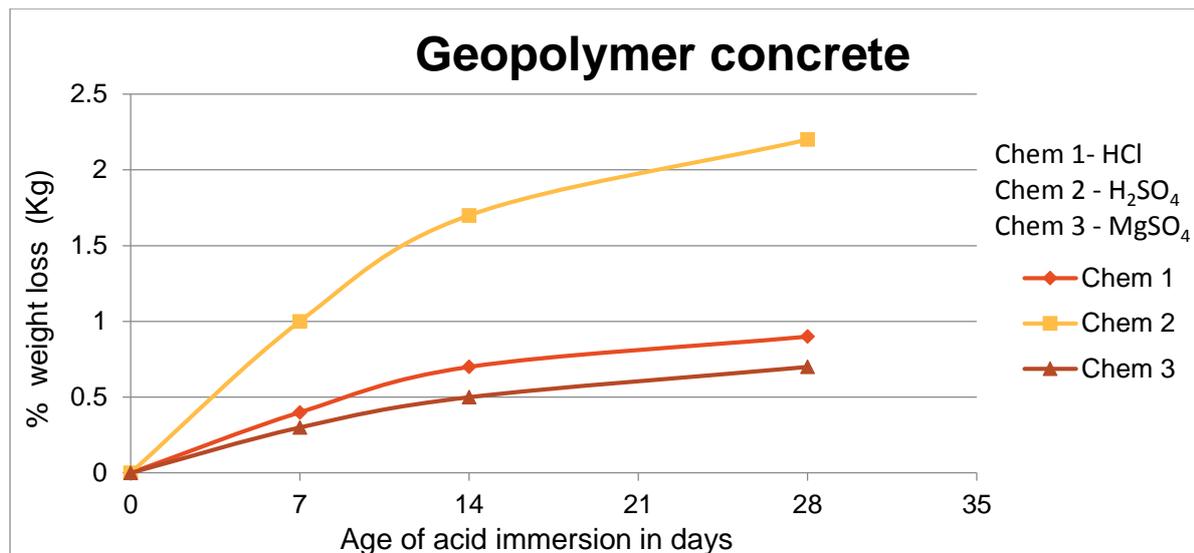
Table: 6 Geopolymer concrete

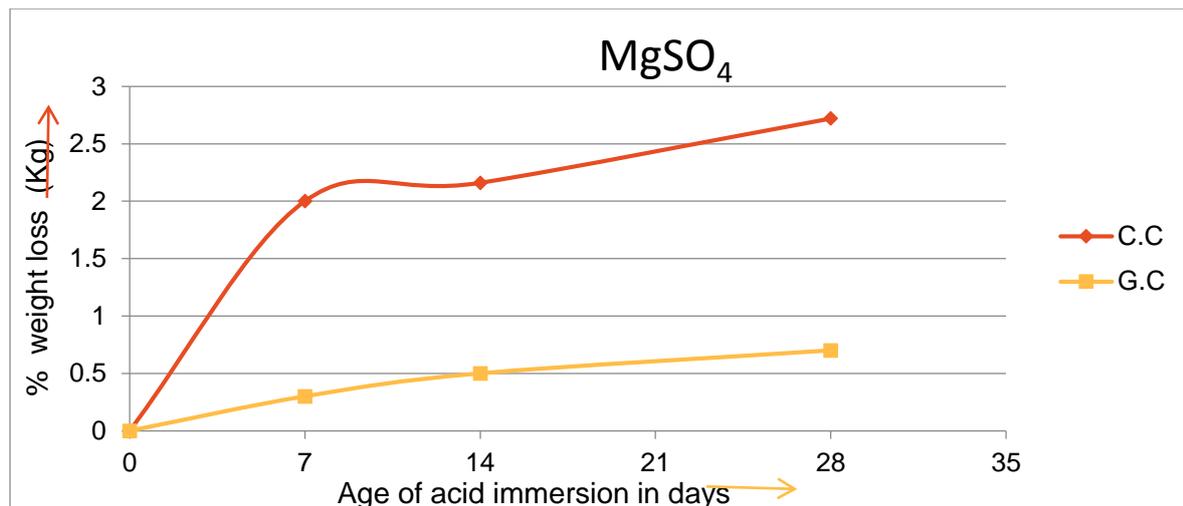
S.No	Type of Acid	% Weight loss of concrete cubes after acid immersion		
		Age of acid immersion in days		
		7	14	28
1	Hcl	0.4%	0.7%	0.9%
2	H ₂ SO ₄	1.0%	1.7%	2.2%
3	MgSO ₄	0.3%	0.5%	0.7%

Graphs









IV. CONCLUSIONS

Geopolymer concrete mixes resisted acid attack in a better way as compared to conventional concrete at all ages of exposure to HCl, H₂SO₄ and MgSO₄.

1. It is observed that the percentage loss of Compressive strength of all Geopolymer Concrete mixes are considerably lower than that of Conventional concrete mixes at all ages of acid exposure for all the three acids
2. It is also observed that the maximum loss of compressive strength and weight occurs in case of H₂SO₄ acid immersion as compared to HCl and MgSO₄ acids .
3. The loss of compressive strength of conventional concrete is almost double the loss of compressive strength of geopolymer concrete in H₂SO₄ acid immersion at all ages.
4. The percentage weight loss of Conventional concrete is more when compared to Geopolymer concrete. This is true for all the acids tried in this investigation.
5. It is observed that the loss of compressive strength of Geopolymer concrete is more when compared to conventional concrete in MgSO₄ acid immersion. So Geopolymer concrete is sensitive to MgSO₄ acid.
6. The weight loss of Geopolymer concrete is very low when Geopolymer concrete mixes are exposed to 5% acid attack.

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AUTHOR DETAILS

GSV Brahammaji Rao was born in Anakapalli, A.P, India, in Year 1992. He received the Bachelor degree in Civil Engineering from the University of JNTU, Kakinada, in 2013 and the Pursuing Masters in Structural Engineering in KITS, Divili, University of JNTU, and Kakinada, both in Civil Engineering.



P.Venkata Muthyalu was born in Avinigadda, A.P, India, in Year 1988. He received the Bachelor degree in Civil Engineering from the University of JNTU, Kakinada, in 2009 and the Masters in Geo-Technical Engineering from the University of JNTU, Kakinada, in Year 2011, both in Civil Engineering. Presently he is working as Assistant Professor & HOD in Civil Engineering Department in Pragati Engineering College, Kakinada, AP

