

Durability of geopolymer concrete exposed to acidic environment – a review.

Durabilidad del hormigón geopolimérico expuesto a un ambiente ácido: una revisión.

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ABSTRACT

Acids attack concrete by dissolving both hydrated and unhydrated cement compounds as well as calcareous aggregates and the subsequent chemical reaction forms water soluble calcium compounds which are then leached away. The aggressiveness of the reaction depends on the pH of the acidic medium and the types of salts formed. Concrete pipes made of ordinary portland cement (OPC) carrying sewage water have always the presence acidic solutions in it. They deteriorate and service life of the pipes is affected along with the increased maintenance costs and that process cause environmental impacts. Geopolymer binders are novel binders that relies on alumina silicate rather calcium silicate bonds for structural integrity so they have been reported as being acid resistant. Those could be produced by the chemical action between alumino-silicate material such as fly ash(FA), granulated blast furnaces slag (GGBS), metakaoline or silica fume with alkaline solutions like sodium silicate or sodium hydroxide. Geopolymers show superior performance in terms of corrosion and fire resistance due to the absence of water and calcium in their structure. Utilization of waste materials like FA and GGBS makes geopolymer concrete (GPC) an environment friendly construction material. This review paper looks in to the effect of various acids such as sulphuric acid, acetic acid, nitric acids on durability properties of OPC specimens, GPC specimens and GPC composite specimens when immersed in acidic solutions for certain period. The performance of geopolymer is

analysed by the visual inspection and studying the parameters like weight loss, loss in compressive strength and maximum depth of penetration.

Keywords- Geopolymer concrete, Sodium hydroxide, sodium silicate, metakaoline, silica fume, alumina silicate

RESUMEN

Los ácidos atacan el hormigón disolviendo los compuestos de cemento hidratados y no hidratados, así como los agregados calcáreos, y la reacción química subsiguiente forma compuestos de calcio solubles en agua que luego se lixivian. La agresividad de la reacción depende del pH del medio ácido y de los tipos de sales formadas. Las tuberías de hormigón hechas de cemento Portland ordinario (OPC) que transportan aguas residuales siempre tienen la presencia de soluciones ácidas. Se deterioran y la vida útil de las tuberías se ve afectada junto con el aumento de los costos de mantenimiento y ese proceso genera impactos ambientales. Los ligantes de geopolímero son ligantes novedosos que se basan en enlaces de silicato de alúmina en lugar de silicato de calcio para su integridad estructural, por lo que se ha informado que son resistentes a los ácidos. Aquellos podrían ser producidos por la acción química entre material de aluminosilicato como cenizas volantes (FA), escoria granulada de altos hornos (GGBS), metacaolina o humo de sílice con soluciones alcalinas como silicato de sodio o hidróxido de sodio. Los geopolímeros muestran un rendimiento superior en términos de resistencia a la corrosión y al fuego debido a la ausencia de agua y calcio en su estructura. La utilización de materiales de desecho como FA y GGBS hace que el concreto geopolímero (GPC) sea un material de construcción amigable con el medio ambiente. Este artículo de revisión analiza el efecto de varios ácidos como el ácido sulfúrico, el ácido acético, los ácidos nítricos en las propiedades de durabilidad de las muestras de OPC, muestras de GPC y muestras compuestas de GPC cuando se sumergen en soluciones ácidas durante cierto período. El desempeño del geopolímero es analizado por inspección visual y estudiando parámetros como pérdida de peso, pérdida de resistencia a la compresión y profundidad máxima de penetración.

Palabras clave: hormigón geopolímero, hidróxido de sodio, silicato de sodio, metacaolina, humo de sílice, silicato de alúmina.

INTRODUCTION

Durability of concrete may be defined as the ability of concrete to resist weathering action, chemical attack, and abrasion while maintaining its desired engineering properties. Different concretes require different degrees of durability depending on the exposed environment and desired properties. Concrete ingredients, their proportioning, interactions

between them, placing and curing practices, and the service environment determine the ultimate durability and life of the concrete.

Concrete is resistant to most natural environments and many chemicals. However, acids attack concrete by dissolving the cement paste and calcium-based aggregates resulting in leaching of acid-susceptible constituents, mainly calcium hydroxide, from the cement paste of hardened concrete. This action results in an increase in capillary porosity, loss of cohesiveness and eventually loss of strength accompanied by crack formation and eventually disintegration, especially for the structures associated with water pressure.

Development of new alkali activated binders with longer durability is needed in the interest of addressing the topic of disintegration of concrete structures made of OPC. Geopolymers are increasingly receiving popularity as novel binders and are emerging as an alternative to OPC binders. The superior performance of geopolymer binders compared with portland cements in terms of corrosion and fire resistance is attributed to the absence of water and calcium in their structure. Investigation of the relative changes in the chemical composition of the corroded layer with the aid of electron probe micro-analysis revealed that there exist a deposition of gypsum crystals in the corroding matrix, when geopolymers are exposed to low and high concentrations of sulphuric acid. These crystals arrest the process of subsequent deterioration from the corrosion effect.

The present work reviews the works done for evaluation of the response of GPCs and their composites when exposed to various acids for a certain period of time. This paper discusses changes in mass, compressive strength, depth of penetration of acid and visual appearance of the specimens as a measure of the material's resistance against acid. The findings discussed in this review paper will be useful in determining durability and hence the applicability of geopolymer materials and their composites for use in acidic environments.

GEOPOLYMER CONCRETE

Geopolymers are prepared by the chemical reaction between alumino-silicate materials and alkaline activators [Davidovits J;2011]. The alumino-silicate binders are ground granulated blast furnace slag, fly ash, micro silica etc. The alkaline activators generally used are sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide ($\text{Ca}(\text{OH})_2$), sodium silicate (Na_2SiO_3), etc. The geopolymerization process consists of dissolution, reorganization, and condensation and polymerization process. Geopolymerization is an exothermic reaction and be represented as follows [Davidovits J;1994]:

due to sulphate attack for OPC specimen is found to be more than that of fly ash based geopolymer concrete [Albitar M et.al;2017]. The chloride resistance of fly ash based GPC with 20% silica fume after 90 days of exposure to 5% sodium chloride (NaCl) solution was evaluated [Francis N. Okoye et.al;2017] and there was no erosion or deterioration on the surface. In terms of weight loss and compressive strength loss of GPC samples were found less than that of M40 OPC specimen. The durability properties like sorptivity, immersed absorption, chloride penetration of fly ash based geopolymer with recycled coarse aggregates (RCA) are superior to OPC concrete containing same amount and type of RCA [Faiz Uddin Ahmed Shaikh;2016]. This is due to the refined microstructure of GPC with RCA than OPC. GGBFS based geopolymer has superior durability properties in terms of chloride ion penetration, sulphate attack than the FA based GPC and OPC [Ahmet Emin Kurtoğlu et.al;2018]. According to Jena S et al. fly ash based GPC replaced with 5% of silica fume has 81.67%, 59% and 65% higher compressive strength than the control mix when exposed to acid, sulphate and chloride solution, respectively.

According to Reddy D V et al., FA based GPC in marine environment is more homogeneous and well bonded to the aggregates than OPC and it has corrosion based improved crack resistance and long term durability. It is found that the geopolymerisation behavior, physical, mechanical properties, and fire resistance characteristics of fly ash, granulated blast furnace slag and calcined clay -based GPCs are strongly dependent upon the chemical composition of the binders [Saxena S K e.al;2017]. Geopolymer mortars made from the different binder sources showed good fire resistance up to 600°C but after that the fire resistant property decreased. Fly ash based GPC with silica fume had the maximum fire resistant property at 800°C and 1000°C. These geopolymers have great potential for engineering applications particularly as a fire resistant material. Partial substitution of GGBFs with 15 % air cooled slag (ACS) increases the thermal stability of GPC up to 1000°C [Khater H M;2014].

DURABILITY OF GEOPOLYMER CONCRETE IN ACIDIC ENVIRONMENT

Valencia-Saavedra W G et al. investigated the performance of FA-based GPCs exposed to acetic and sulfuric acids. The raw materials used were FA, GGBS and OPC for the experiment. Concrete cubes of 50.8 mm per side were prepared and after a curing period of 28 days, cubes were immersed for a period of up to 360 days in 1 M solution acetic acid ($\text{CH}_3\text{-COOH}$, pH \sim 2.4) and sulfuric acid (H_2SO_4 , pH \sim 0). It was found that OPC concrete cube lost 98% of its strength after immersion of 360 days in acetic acid solution while FA/GGBS and FA/OPC lost strengths 66% and 81% respectively. At the end of exposure period, the lowest weight loss was exhibited by FA/GGBS specimens (6.44%) and highest for OPC specimens (16.30%) in acetic acid solutions and the specimens immersed in sulfuric acid the OPC specimens show a weight loss of 18.04 % while the

GPC specimens show around 3% only. The visual inspection also shows greater deterioration on OPC based samples.

In their investigation, Khan H A et.al. placed 50mm mortar cubes of FA and GGBFS based geopolymer and sulphate resistant cement in sewer chamber to analyze the deterioration after biogenic corrosion and another set of samples was immersed in 1.5% sulphuric acid solution. Geopolymer mortars showed smooth cubical surface with minor cracks near edges and sulphate resistant cement mortars showed more degradation and loss of 2-3 mm from the surface after two years of exposure in sewer chamber. The loss in mass and compressive strength was much higher in sulphate resistant cement mortars as compared to geopolymer mortars. Mass loss of around 7.5%–19.2% was observed in sulphate resistant cement mortars due to surface spalling and crack propagation between aggregate and matrix, whereas in geopolymer mortars this mass loss ranged from 3.5% to 7.4%. Sulphate resistant cement mortars experienced a compressive strength loss of 43.3%–67.6% respectively. For geopolymer mortars this reduction in strength was only 15%–56% confirming that the degradation in sulphate resistant cement mortars was much more prominent compared to geopolymer mortars. The corrosion depth was more in geopolymer mortars than sulphate resistant cement mortars due to the greater volume of permeable voids in geopolymer mortars.

Mehta A et al. conducted experiments on the sulfuric acid resistance of FA based geopolymer concrete. OPC is added in different percentages as a FA replacement and the specimens are immersed in 2% sulphuric acid for 365 days. The deterioration is studied based on the in terms of weight loss and compressive strength loss. As the OPC content increases the weight loss of the specimen also increases. It was observed that weight losses of 4.28, 4.28, 5.83, 9.47 and 15.48% at 365 days for the specimens with 0, 10, 20 and 30% respectively. The compressive strength loss for specimens beyond 10% OPC was more than those for 0% and 10% for 365 days in acid immersion. The reason for this could be the increase in OPC beyond 10% formed more calcium hydrated products and created extra nucleation sites for the acid attack in the geopolymer system and form additional calcium sulfates.

Bakharev T et al; 2013, studied about the resistance of alkali-activated slag concrete to acid attack. The test was conducted by immersing alkali activated slag concrete in acetic acid solution having a $p^H= 4$. The control specimen was OPC. OPC had 47% strength reduction and alkali activated concrete specimen has 33%. The depth of penetration for OPC was 22 mm and that of alkali activated concrete specimen is 16 mm.

Bakharev T studied about the resistance of geopolymer materials to acid attack. The resistance of FA based GPC specimens in comparisons with OPC and OPC+20% FA specimens were investigated by immersing cylindrical specimens ($\square 25 \times$

50 mm) in solutions of 5% acetic and sulfuric acid. p^H of sulfuric acid was 0.8 and for acetic acid 2.4. Geopolymer specimens had very small change in appearance after immersing 150 days in both acids. OPC and OPC+20% FA specimens underwent severe deterioration at the end of 5 months. OPC and OPC+20% FA lost compressive strength by 91 and 84% at the end of 150 days of immersion period where as the strength loss of GPC specimens were in the range of 38 to 60% depending upon the activator solution.

Ariffin M A M et al;2013, studied the sulfuric acid resistance of blended ash geopolymer concrete. The GPC for the experiment was prepared by blending ash of pulverized fuel ash (PFA) and palm oil fuel ash (POFA) and activated with alkaline activators. The acid solution was 2% sulfuric acid. The durability test was conducted 18 months. The control mix used in this experiment was OPC. After 18 months of exposure, the GPC specimen had a weight loss of 8% compared to the 20% weight loss of OPC specimen. The OPC had a compressive strength loss of 68% against 35% of GPC.

Khater H M; 2014, studied the effect of thermal and acid exposure on alkali activated slag geopolymer. The geopolymer material on study was prepared from GGBS, air cooled slag (ACS), silica fume (SF), and cement kiln dust (CKD) and the activator is the 6% of equal mix from sodium hydroxide and sodium silicate. It was found that GPCs made partial replacement of GGBS with SF has most resistance to acid attack.

Sonal Thakkar et al;2014, studied the resistance of geopolymer concrete with fly ash and slag to sulphate and acid attack. The GPC specimens are immersed in 5% sulfuric acid and compared with OPC specimens. The change in mass for fly ash based geopolymer concrete after 90 days of acid exposure is 0.51% where as for slag based geopolymer concrete is 0.92%. The control concrete specimen had serious loss in mass of 15.51%. The compressive strength losses were 7.53%, 7.01% and 36.61% for fly ash based geopolymer, slag based geopolymer and OPC specimens respectively.

Madhan Gopal K et al;2013, investigated on behavior of FA based geopolymer concrete in acidic environment. Class F FA based GPC was prepared for the experiment and the specimens were compared against immersion in 5% acid solutions of sulfuric acid (H_2SO_4) and hydrochloric acid (HCL). The specimens were heat cured for 24 hours at $60^{\circ}C$. The specimens were cured for 28 days in ambient temperature and immersed in acidic solution and tested for mechanical properties afterwards. It was found that the weight loss of OPC specimens after 28 days in HCL and H_2SO_4 are 3.76% and 8% respectively where for GPC the weight losses were 0.9% and 2.2% respectively. Compressive strength of OPC specimen in HCL lost 8.67% and the loss in H_2SO_4 is 57.6%. The GPC in HCL lost its strength by 14.06% and in H_2SO_4 the loss is 27.5% after 28 days.

COMPARISON OF RESULTS

A comparison of loss in weight and loss in compressive strength of OPC and GPC immersed in sulphuric acid solution observed in various studies conducted by the authors

are tabulated below. The experiments are conducted with different concentrations of sulphuric acid with different exposure period.

Table 1: Comparison of loss in Weight and loss in compressive strength of OPC and GPC in immersion of sulphuric acid solution

	Authors							
	Valencia-Saavedra W G et al.		Ariffin M A M et al.		Sonal Thakkar et al.		Madhan Gopal K et al.	
	GPC	OPC	GPC	OPC	GPC	OPC	GPC	OPC
Loss in Weight	3%	18.04%	8%	20%	0.51%	15.51%	2.20%	8%
Compressive strength	66%	98%	35%	68%	7.53%	36.61%	27.50%	57.60%

From the results it is clearly understood that GPC specimens has superior durability properties in acidic medium as indicated by their low loss in weigh and loss in compressive strength.

CONCLUSIONS

The following conclusions were made from the literature review,

- The calcium silicate gel system in OPC deteriorates in presence of acids causing the degradation of binder system by forming poorly cohesive and expansive calcium salts like gypsum.
- Sulfuric acid attack converts alumino-silicate gel in GPC in to a soft sponge like substance with sulphur and silicon compound but still has binding properties.
- Exposure to acetic acid and sulfuric acid results a complete destruction of OPC specimens while FA/GGBS and FA/OPC specimens were able to retain some of the mechanical properties
- Acid resistance of GPC is found greater than portland pozzolana cement concrete
- Durability in terms of mass loss, loss in compressive strength and surface disintegration for Class F fly ash geopolymer mortars in natural sewer condition and sulfuric acid condition are found better than sulphate resisting cement mortars.
- The acid resistance fly ash based GPC and GGBS based GPC are almost same and the loss in compressive strength is slightly less in GGBS based GPC.
- The acid resistance of GGBS based GPC is higher than that of blended GPCs with GGBS and fly ash. The increase in percentage of fly ash in blended GPCs increases the weight loss and compressive strength loss.
- The depth of corrosion and penetration of acid attack depends on the pH of the medium and mineralogy of the concrete specimen.
- The presence of sodium hydroxide and sodium silicate as alkaline activators contributes to the acid resistance of GPC.
- The selection of aggregates for GPC is critical for its acid resistance. High purity

siliceous aggregates are recommended for making GPC.

- The increase in Ca content in GPC increases the deterioration due to the forming of more calcium sulphate.
- Durability of GPC in acidic environment is related to the depolymerization of aluminosilicate compounds and there by liberating silicic acid.
- The alkaline solution has a significant role in the deterioration GPC compounds in acidic media. Presence of sodium hydroxide results an ordered polymerization while sodium silicate solution results in an amorphous structure, thereby increases the stability of GPCs prepared with sodium hydroxide.
- Addition of GGBS in to FA based geopolymer improves the durability properties of the geopolymer in acidic environment.

In summary, the paper reviews the resistance of geopolymer concrete exposed to different acidic environment. It is evident that GPC has excellent durability properties against acids and the acid resistance is way better than OPC. GPC can be considered as an excellent sustainable alternative construction material where acid attack is expected such as in sewer lines.

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