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DETERIORATION OF ORDINARY PORTLAND CEMENT AND FLY-ASH BASED GEO-POLYMER CONCRETES DUE TO SULFATE ATTACK UNDER THE ACTION OF SULFURIC ACID AND WASTEWATER

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ABSTRACT

Corrosion in concrete sewers and wastewater treatment plants has been a major problem but this issue has not been resolved satisfactorily yet. Generally, deterioration happens due to sulfuric acid reaction with treatment units and sewer materials. Geo-polymer binders especially fly ash (FA) is an acid resistant and can be used as a substitute binder for sewer construction. This research work highlights the laboratory results of fly ash based geo-polymer concrete and effects on its durability under sulfuric acid exposure. Class 'F' fly ash was used in the preparation of samples that were properly cured for 28 days at room temperature. After curing, specimens were immersed in three types of sulfate containing solutions to check corrosion.. These sulfate containing solutions include static sulfuric acid, dynamic wastewater and static wastewater. Samples were tested at 28, 45 and 60 days after immersing in different type of solutions to find the corrosion depth. By visual inspection the corrosion depth and residual compressive strength were observed according to the modified ASTM C267& C39 respectively. Reaction products of gypsum remained on the surface of concrete samples absorbed in diluted sulfuric acid, while reaction products of gypsum were not seen on the surfaces of concrete samples absorbed in static as well as dynamic wastewater. Static wastewater also produced corrosion but in a limited fashion, it causes only surface weathering. The obtained results are strongly confirming that geo-polymer concrete samples are showing great resistant to sulfuric acid solution. Moreover, geo-polymer samples were also showing reasonable load carrying capacity after entire section had been neutralized by sulfuric acid.

KEYWORDS: *Geo-polymer, Concrete durability, Fly ash, Acid resistance, Wastewater concrete structures, Sewers*

INTRODUCTION

The deterioration of wastewater conveyance and treatment infrastructures has long been a cause for concern but the issues remained unknown for many years. Wastewater treatment systems are traditionally designed to resist high levels of sulfate attack but subjected to a considerably more aggressive form of deterioration under sulfuric acid corrosion[1]. Sulfates in wastewater are converted to hydrogen sulfide (H_2S) gas which is then converted to sulfuric acid. Sulfuric acid reacts with calcium hydrates to form gypsum which on further reaction with calcium aluminates produces ettringite[2-3]. Sulfuric acid is formed by more dissolution of hydrogen sulfide gas, thus more gypsum will be produced and hence more deterioration will occur, therefore, dynamic wastewater attacks much severely than the static one[3-4].

Fly ash can be used in order to reduce sulphate attack under different circumstances[4]. Several research works have been conducted on concrete deterioration due to sulphate attack. Most of research works are also presenting different cement replacement materials in different ratios and prone to different concentrations of acids. Acid resistance tests were also conducted but no universally accepted methods or specifications for such tests are available. Hence it is very difficult to draw conclusions. There is a need to make simulative studies of concrete having fly ash and identification of different parameters to determine resistance of concrete to sulphate attack.

The sulfate attack on wastewater concrete structures is a very common phenomenon and creating a lot of problem in the field. The use of fly-ash as cement replacement material may improve the strength

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and resistance against sulfate attack under acidic environment. Being a developing country, Pakistan is seriously facing these issues only a very few research articles are addressing the issue under the indigenous environment. This research work is addressing the behavior of OPC and FA concretes under the attack of sulfuric acid and wastewater while considering the indigenous environmental conditions.

LITERATURE REVIEW

Sulfates and acids are found in different forms in nature, e.g., as humic acid in organic form or these can be found in industrial wastes. Liquids having pH less than 6.5 can attack concrete. Concrete particles are held together by alkaline compounds and it cannot resist the strong acid attack. Hence the ultimate result of sustained attack is disintegration and destruction of the concrete. The mechanism of attack involves the reaction between cement hydrates and acid resulting in the formation of calcium salts of that acid. The dissolution of these salts tends to further exposure of cement hydrates to attack. Damaging rate is controlled by solubility of calcium salts. Therefore flowing wastewater yields more deterioration rather than the static one. Acid rain may cause the surface weathering of concrete as it mainly consists of sulphuric acid and nitric acid. Reduced content of calcium hydroxide incorporating fly ash has been found to be much beneficial in reducing sulphate attack.

High values of Biological Oxygen Demand (BOD), high concentration of sulfate and sulfide, extreme temperatures, lofty H_2S gas flumes, and low wastewater pH are the factors that promote sulphate attack. These contributory factors are seriously affecting the concrete structures of wastewater treatment plants (WWTPs). Concrete deprivation has been recorded in a limited fashion in aeration tanks during wastewater treatment, in septic tanks and in primary influent channels[5-8]. The corrosion has been recorded just over the effluent line at WWTPs. It is considerable in the previous investigational studies to understand, the deprivation of sewer lines has also shown the similar trend like WWTPs[4,9]. A research work was carried out to determine the depth affect on concrete structures under sulfate attack by collecting different core samples from sewage treatment plant at different components[10].

Sulfuric acid is seriously acting as a corrosive agent for sewer lines and as well as WWTPs[10]. Reaction by the sulfuric acid is presenting a joint sulfate-acid reaction and hydrogen ion concentrations are generating a dissolution effect[3-4]. In the first step when the sulfuric acid reacts with a cementations material, a reaction between acid and calcium hydroxide forming calcium sulfate as shown in the following equation 1:

$$Ca\,(OH)_2 + H_2SO_4, \rightarrow CaSO_4 + 2H_2O \qquad (1)$$

It is subsequently hydrated to form gypsum ($CaSO_4 \cdot 2H_2O$) and then its presence on the surface of RCC/PCC pipes presents a white soggy powder without any cohesive properties[2,4]. During the same reaction, produced gypsum would be able to react with calcium aluminates hydrate (C_3A) to form an expansive product like ettringite as shown in the equation 2:

$$3CaSO_4 \cdot 2H_2O + 3CaO \cdot Al_2O_3 + 26H_2O\ ’\rightarrow$$
$$(CaO)_3 \cdot (Al_2O_3) \cdot (CaSO_4)_3 \cdot 32\ H_2O\ \text{(Ettringite)} \qquad (2)$$

Ettringite can be observed in lower sections of concrete structures under high pH[3] and where as a minor ettringite can also be observed on damaged concrete pipes[2]. Findings from the previous researches are clearly indicating that there is a diverse relationship between concrete corrosion and nature of wastewater. Common variables include environmental conditions, the nature of attack and the physical results of the attack on concrete. It is also explained in literature that how a model-shift is required for a proper concrete design, converting from a traditional approach to performance-based design. Therefore it is important to consider the aggressiveness of wastewater environment to concrete structures during their service[11-12].

It was discovered during the previous researches that concrete sewer under sulfuric acid attack are producing white deposits, those are moist, flaky and removable from the concrete surface[4,13]. At early stages of concrete corrosion sulfate ions are being released by the special type of bacteria. Further, in wastewater the presence of dissolve oxygen expedite whole process to generate hydrogen sulfide[13-14]. Generally, the pH value of normal sewage is 5-6 and presenting weak acidic behavior but under low values of pH, the produced amount H_2S can be recovered from the top surface of wastewater. A slim film of dampness survives on the face of the concrete pipe exposed to the atmosphere and the hydrogen sulfide gas gets dissolved. Hydrogen sulfide (H_2S) is divided into HS^- or S^{2-} ions which further attract more H_2S into the damp deposit[15]. Research illustrates that the amount of the hydrogen sulfide (H_2S) under the damp layer enhances as the pH value inside the concrete pipe starts decreasing[16]. When oxygen is present, the H_2S responds to form essential sulfur or moderately oxidized sulfur variety which can be seen in the deterioration products placed on the concrete face[9,17]. The acid behavior of the wastewater must be controlled to overcome the concrete corrosion problems. Further, the biological attack on wastewater concrete structures has also showing significant impacts on concrete deterioration. Removal of loosely adhering particles may be important to minimize biological activity[18].

MATERIALS AND METHODS

Wastewater corrosion in PCC and RCC sewer has become a major issue. It creates problems in wastewater treatment plants as well. Therefore this research was conducted to describe the comparison of corrosion depth and compressive strength using different water-binder (W/B) ratio with different binder materials and fly ash was selected as mineral admixture. Different medium of exposure were selected which are the most common in Pakistan. 1.0 mol/liter static sulfuric acid, the static wastewater and dynamic wastewater were selected as medium of exposure. Concrete cubes of 150×150×150 mm in size were caste with water-binder ratios of 0.5, 0.57, and 0.65. These W/B ratios were selected while considering the economic aspects in developing countries like Pakistan. The cubes specimens of size 150×150×150 mm were used because they comply with ASTM C-39 standard to measure the compressive strength.

Medium sized graded sand collected from local quarry at Lawerencepur was utilized. The coarse aggregates collected from another local mine from Margallah near Taxila having maximum size of 20 mm and minimum size of 10 mm was used. The physical properties of consumed materials are shown in Table 1.

Table 1: Physical Properties of Materials

Materials	Properties
Cement	Ordinary Portland Cement Density:3.04 g/cm^3
Fly Ash	Density:2.10 g/cm^3
Fine Aggregates	Lawrencepur Sand Pit Specific Gravity:2.27 g/cm^3 Fineness Modulus: 2.72
Coarse Aggregates	Margalla Crushed Stone Specific Gravity:2.69 g/cm^3 Fineness Modulus: 5.91

EXPERIMENTAL METHODS

The concentrations of sulfuric acid solutions in immersion tests were 1.0 mol/L for concrete specimen. The immersion tests contain three types of solutions. Specimens were immersed in static sulfuric acid solution, in dynamic wastewater and in static wastewater. The initial depth of any cube was considered the linear dimension of any one side e.g. 150 mm. After immersion tests were started, corrosion depth was measured after 28, 45 and 60 days. The corrosion depth is defined as “the distance between the initial surface of the concrete and the current surface i.e representing the final eroded surface”. Before every measurement intentional removal of deteriorated zone on surface was not carried out in order to prevent specimens from any strength loss due to gypsum and ettringite removal collected at the surface of specimens. These test methods are intended to evaluate the chemical resistance of resin, silica, silicate, sulfur, and hydraulic materials, grouts, monolithic surfacing, and polymer concretes under anticipated service conditions. ASTM C267-01 provides for the determination of changes in the following properties of the test specimens and test medium after exposure of the specimens to the medium:

- Weight of specimen,
- Appearance of specimen,
- Appearance of test medium, and
- Compressive strength of specimens.

RESULTS AND DISCUSSIONS

(a) Corrosion effects due to sullphuric acid and wastewater

The corrosion depth of concrete specimens immersed in 1.0 mol/L of sulfuric acid solution was more.

For specimens with each W/B ratio, the corrosion depth of concrete in dynamic wastewater was greater than in static waste water. Reaction products of gypsum remained on the exterior faces of concrete samples placed under sulfuric acid solution, while nothing was seen on the face of concrete samples engrossed under dynamic as well as static wastewater as shown in following Figures 1, 2 and 3.

Figure 1: Sample cubes under sulfuric acid attack

Figure 2: Sample cubes under static wastewater

Figure 3: Sample cubes under dynamic wastewater

Sulfuric acid penetrates into concrete cubes and reacts with calcium hydroxide of cement hydrates to produce gypsum[19]. It causes the volume of concrete to increase largely which causes the expansions of reaction products resulting in corrosion. Concrete with the high water cement ratio contain larger and more pore than that with the low water cement ratio. These pores are actually the capacity to absorb expansions caused by the production of gypsum. Hence concrete with the high W/B has a larger capacity to absorb the expansions of gypsums. In other words concrete with low W/B ratio corrode earlier than that with the high W/B. Concrete deterioration occurs only in the surface portion of specimens. It is all because the reaction of gypsum in the surface portion is faster than the penetration of sulphate ions into that specimen. Hence surface portion is a main field of reaction of sulfuric acid. Therefore, specimens immersed in static wastewater eroded larger than those immersed in dynamic wastewater. Since the flow of solution resisted the reaction product of gypsum.

(b) Resistance to Corrosion by the addition of Fly Ash

The corrosion depths of the samples were measured at 28, 45 and 60 days excluding curing period. The corrosion depth of concrete samples having fly ash was smaller than the samples without fly ash. Less calcium hydroxide was observed in concrete samples having fly ash as compare to concrete samples without fly ash. To investigate properly up to 30% of binding material was replaced with fly ash during the experiment work. The corrosion depth in concrete specimens containing fly ash was the smallest one. Hence the production of gypsum is the main cause of concrete deterioration due to sulfuric acid attack. From the obtained results, it is clear that compressive strength of OPC concrete is least in static sulfuric acid when W/B ratio was kept 0.5; it gradually increases for W/B ratios of 0.57 and 0.65. Same is the case with Geopolymer concrete.

From the summarized results in Table 2, it is clear that strength of OPC and Geopolymer concrete is least in static sulfuric acid solution and was high when medium was static wastewater. The strength of cubes being soaked in dynamic wastewater lies in between of the above mentioned mediums. Figure 4, 5 and 6 are presenting the compressive strength of the samples at 28, 45 and 60 days. The same results are also shown in Table 2 as well. Different combinations of fly-ash with OPC are showing highest compressive strength under static wastewater at 28, 45 and 60 days. The samples prepared with OPC only are showing the lowest compressive strength under static sulfuric acid attack at 28, 45 and 60 days. The prepared samples with OPC and FA are also showing reasonable compressive strength under the influence of dynamic wastewater. The corrosion depths of different specimens are shown in Table 3. These corrosion depths are also explained in Figures 7, 8 and 9.

Table 2: Comparison of compressive strength of concrete with & without FA using different W/B ratios & medium of exposure.

Sr. No.	W/B Ratio	Medium of Exposure	Compressive Strength (MPa) after immersion					
			OPC Concrete Cubes			OPC+FA Concrete Cubes		
			28 Days	45 Days	60 Days	28 Days	45 Days	60 Days
01	0.50	Sullphuric Acid (Static)	15.6	18.9	21.1	21.8	31.6	32.4
		Wastewater (Dynamic)	23.1	23.6	24.4	29.3	32.0	33.3
		Wastewater (Static)	25.6	26.2	27.1	31.4	36.4	37.6
02	0.57	Sullphuric Acid (Static)	12.7	15.6	18.0	19.4	20.4	21.8
		Wastewater (Dynamic)	17.9	18.4	19.1	26.4	27.6	30.0
		Wastewater (Static)	23.1	23.5	24.9	27.3	38.1	36.2
03	0.65	Sullphuric Acid (Static)	9.4	11.1	12.2	17.8	19.1	20.4
		Wastewater (Dynamic)	10.7	12.4	14.7	23.9	24.9	25.9
		Wastewater (Static)	21.6	22.2	23.1	27.1	31.1	35.8

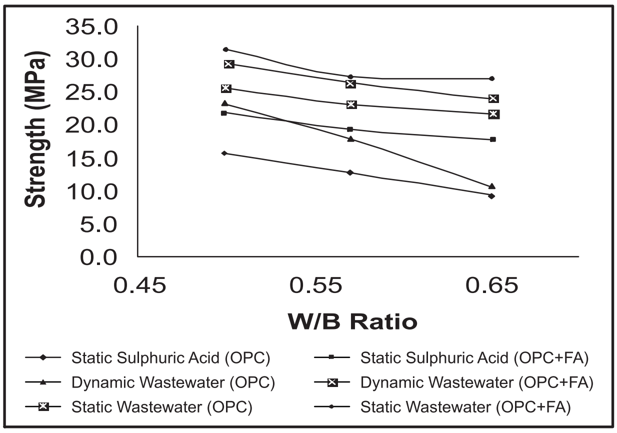

Figure 4: Comparison of compressive strength after 28 days of immersion with & without FA using different W/B ratios & medium of exposure.

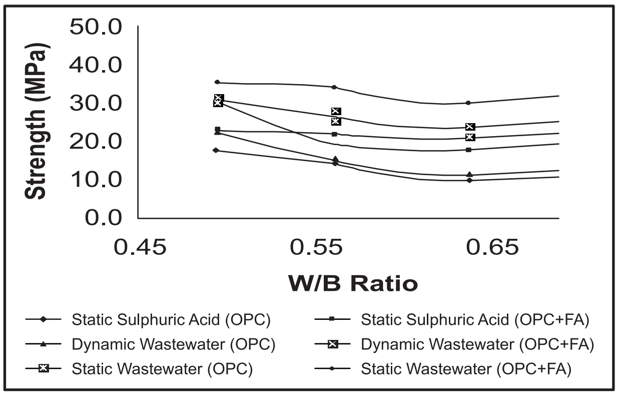

Figure 5: Comparison of compressive strength after 45 days of immersion with & without FA using different W/B ratios & medium of exposure.

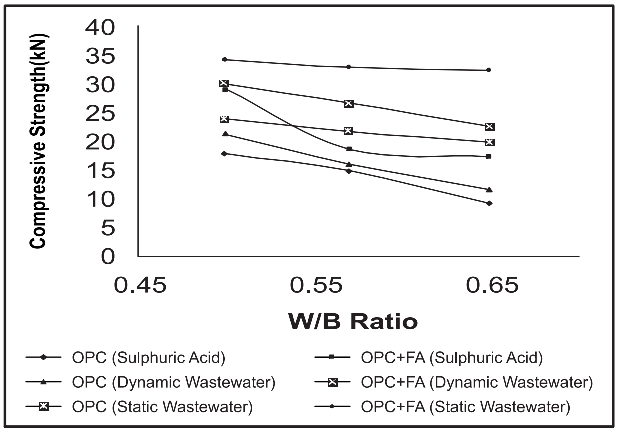

Figure 6: Comparison of compressive strength after 60 days of immersion with & without FA using different W/B ratios & medium of exposure.

Table 3: Corrosion depths of concrete specimens with & without FA using different W/B ratios & medium of exposure.

Sr. No.	W/B Ratio	Medium of Exposure	Corrosion Depth (mm)					
			OPC Concrete Cubes			OPC+FA Concrete Cubes		
			28 Days	45 Days	60 Days	28 Days	45 Days	60 Days
01	0.50	Sullphuric Acid (Static)	5	7	10	4	5	7
		Wastewater (Dynamic)	0.3	0.5	0.8	0.1	0.2	0.3
		Wastewater (Static)	0.1	0.2	0.4	0.08	0.1	0.2
02	0.57	Sullphuric Acid (Static)	8	10	13	5	6	8
		Wastewater (Dynamic)	0.5	0.7	0.9	0.3	0.4	0.5
		Wastewater (Static)	0.3	0.5	0.6	0.2	0.3	0.4
03	0.65	Sullphuric Acid (Static)	10	12	15	6	7	9
		Wastewater (Dynamic)	1	1.2	1.5	0.5	0.6	0.8
		Wastewater (Static)	0.4	06	0.8	0.3	0.4	0.6

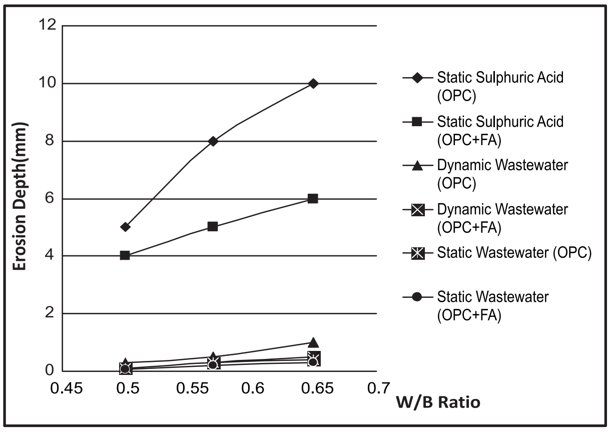

Figure 7: Comparison of corrosion after 28 days of immersion with & without FA using different W/B ratios & medium of exposure.

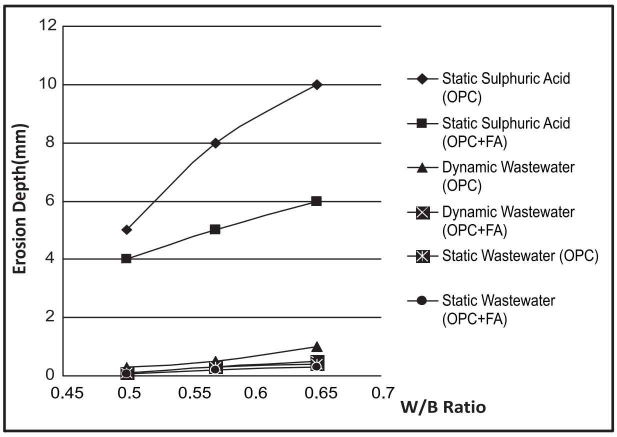

Figure 8: Comparison of corrosion after 45 days of immersion with & without FA using different W/B ratios & medium of exposure.

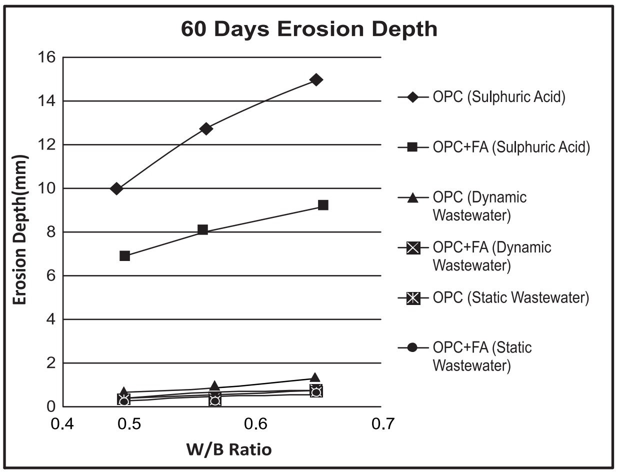

Figure 9: Comparison of corrosion depth after 60 days of immersion with & without FA using different W/B ratios & medium of exposure.

CONCLUSIONS

Concrete deterioration increases by increasing the water binder ratio due to more expansion occurring while decreases by increasing the amount of fly ash as cement replacement. Concrete deterioration due to sulfuric acid attack in geo-polymer concrete having fly ash contents is lesser as compared to ordinary mix concrete after 28, 45 and 60 days of immersion in different medium. Samples containing 30% fly-ash as cement replacement with 0.65 W/B ratio show best result against corrosion under static effect of acidic media. They show 25%, 40% and 43% less corrosion under the exposure of static acidic media in the laboratory after 28, 45 and 60 days of immersion, respectively. In case of dynamic wastewater as medium of exposure, concrete samples containing 30% fly-ash with 0.5 W/B ratio show the best performance. They show 200%, 150% and 167% less deterioration than ordinary concrete samples after 28, 45 and 60 days of immersion in different medium, respectively. Same is the case under static wastewater. From another point of view more corrosion and strength loss occurs in sulfuric acid exposed specimens rather than the immersed in dynamic wastewater as well as static wastewater. Another conclusion was also drawn that dynamic wastewater causes more corrosion and strength loss than the static wastewater at all ages e.g. 28, 45 and 60 days after immersion.

At early stage, the mixing of high percentages of FA in the concrete samples showed low strength but the observed strength for the same samples were high. During the research, under constant water-binder ratio of 0.5 and replacement of some quantity of OPC with FA showed decrease in compressive strength at early stage up to 60 days but after that the compressive strength was significantly improved for the same samples. These conclusions would highlight that ordinary concrete containing fly ash results in the best performance regarding strength and sulfate resistance.

RECOMMENDATIONS

The replacement of cement by fly ash has considerable advantages. It not only increases the strength of concrete, but also reduces sulfate attack in wastewater concrete infrastructures like sewers and wastewater treatment systems. Similarly, it makes concrete more economical as the fly ash is not expensive as compared to cement and it minimizes corrosion. Fly ash also resists sulfate attack much well rather than the ordinary concrete for long durations.

This experimental study investigated that some quantity of OPC can be replaced with a reasonable percentage of fly ash to introduce a durable concrete without compromising the strength. In this study, to investigate the reactions of wastewater with concrete the wastewater was collected from the communal source only. Although, the wastewaters from different sources are presenting different properties, thus the behavior ordinary and geo-polymer concretes may be studied under different types of wastewaters characteristics.

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