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Performance of Self-Compacting Concrete Containing Pozzolanic Materials in Aggressive Environment

Abstract- *The aims of this study is to investigate the resistance of different SCC mixtures to aggressive solutions. The investigation included the type of the cementitious materials (silica fume and high reactivity Attapulguite-HRA) and limestone powder (chalk powder and Al-gubra). The powder content of the mixes was kept constant, 500 kg/m^3. The slump flow, L-box, and V-funnel were performed for mixes in there fresh state. In the present work, the specimens were immersed in sulfuric acid solution with a concentration of 0. 5% up to 289 days after normal curing for 28 days. After concrete has hardened, two types of test are performed. Firstly, destructive tests are conducted including (compressive strength, splitting tensile strength, and modulus of rupture). Secondly, a mass loss as non-destructive test is performed. The results obtained from this work, show that concrete mixes with chalk powder only, had the best resistance to sulfuric acid solution comparable with concrete made with Pozzolanic materials the reduction in compressive strength was 25. 9 %. In addition, concrete mixes with HRA had the worst resistance.*

Keywords- *limestone powder, self-compacting concrete, silica fume, sulfuric acid*

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1. Introduction

Concrete can be attacked by liquids with pH value below 6.5 but the attacks are severe only at a pH below 5.5 [1]. Sulfuric acid fluids are classified as the most aggressive of natural threats to concrete structures. Generally, they arise from industrial operations, but they can be caused by urban areas activities. Acid attack is influenced by the processes of disintegration of the paste constituent. The admixtures in SCC paste can negatively or positively affect its resistance to acid aggression [2]. The deterioration of concrete in acidic environments is influenced by several factors such as the type of cement used, permeability of concrete, and the surrounding environmental conditions. Furthermore, the solubility of calcium salt produced from the acid – base reaction of the cementitious paste and attacking acid is an important factor [3]. Many studies about the possibility of improving the quality and performance of concrete have been accomplished. Dhiyaneshwaran *et al.* [4] used fly ash Class F at different replacement levels, 10, 20, 30, and 40% by weight of cement. After 28 curing, the specimens were immersed in aggressive solution, 1% sulfuric acid, the weight reduction and the compressive strength loss were calculated at the age of 28, 56 and 90 days. The results noticed that, as increasing in fly ash percentages, both the compressive strength loss and the weight reduction of the specimen would be reduced. Chang *et al.* [5] investigated six concretes mixes; contain limestone aggregates and siliceous aggregates. They also used three Pozzolanic materials, slag, fly ash and silica fume. In their work, the concrete specimens were immersed in 1% H_2SO_4 solution. The result from the experimental program shows that, using concrete with cement containing fly ash and silica fume and limestone aggregates performed the best. Monteny *et al.* [6] reported that, in the case of low permeability (high pore densification), the fine pores may contribute an increase the capillary suction resulting in solution which enters deeper into the concrete. In spite of the total amount of solution taken up by the concrete is relatively small, the solution which intervention the concrete, is very aggressive and can dissociates into sulfate ions and due of pore densification, the solution will comes in contact with a larger concrete surface comparable with the same amount of aggressive solution is taking up by concrete in the case of large pores. Increase the surface area of the concrete-contact with the aggressive solution will lead to an increase in the

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reaction products. A study was conducted by Daczko *et al.* as cited by Joorabchian [7] on the performance of concrete, in their work different values of pH in the range of (1 to 7*)* and three admixtures MK, silica fume and an organic corrosion inhibitor (OCI) were used in this study to enhance concrete performance bars against sulfuric acid solutions. The replacement level for silica fume and Metakaolin was 8% in two separate mixes. In this work, the total period of immersion in acid solution was 100 days. The final results of their work demonstrate improved performance of OCI and silica fume concrete, but no such improvement was observed for concrete containing Metakaolin concrete Daczko *et al.* believed that the presence of high percentage of Al_2O_3 in the MK may cause further reaction and corrosion of concrete that is exposed to sulfuric acid. An experimental program was carried out by Senhadji *et al.* [8] to study the influence of different supplementary cementitious materials (silica fume, natural Pozzolan*)* and limestone fine at various replacement levels. The results showed that the addition of limestone powder or natural Pozzolan could improve the acid resistance of mortar, but at different rates depending on the proportion of supplementary cementitious materials. On the other hand, mortars with silica fume are seriously damaged in the sulfuric acid environment. Girardi *et al.* [9] studied the deterioration of concretes mixtures with different cement composition, (Portland limestone, blast furnace slag, silica fume, Pozzolanic cement and Pozzolanic cement with silica fume) to a cycle exposure of sulfuric acid. The result indicated that mixtures containing silica fume exhibited the lowest expansion.

2. Research Significance

Several concrete elements are susceptible to chemical attack of sulfuric acid, including, industrial floors of chemical plants, superstructures, sewage pipe systems, etc. A comprehensive review indicates that there is lack of information on the role of high reactive Attapulguite (HRA) that can be inserted in SCC in such aggressive environment.

3. Materials

The binders used in Table 1 included ordinary Portland cement (OPC), (ASTM C150 – Type 1) [10]. The cement was tested and checked according to IQS 5:1984[11], silica fume (SF) to ASTM 1240-03 [12], high reactivity Attapulguite to ASTM 618-03. The used HRA was prepared by calcinations the Attapulguite powder at 750°C with soaking time of 1/2 hour then left to cool down [13]. Two types of limestone powder (gubra and chalk powder) were used throughout this investigation.

Table 1: The properties for the binders

Oxides	C	HRA	SF	Gu	Ch
SiO_2	20	47.91	96.7	1. 50	2. 24
FeO_3	3. 9	1. 81	0. 07	0. 08	0. 12
Al_2O_3	4. 5	20.94	0. 20	0. 32	0. 42
CaO	62	10.06	0. 54	54. 6	68. 73
MgO	2. 43	47.91	0. 12	0. 27	0. 70
SO_3	2. 03	1. 81	0. 61	<0.07	<0.07
Specific gravity	3. 2	2. 4	2. 13	0. 774	2. 42
Fineness m^2/g	4.37	2. 1	157	2. 48	3. 17

Note: C=cement, HRA= High Reactive Attapulgite, SF=silica fume, Gu = Gubra, Ch= Chalk powder

The binder content was kept compatible to the guidelines for SCC mixture design, i. e. EFNARC [14]. The maximum nominal size for crushed coarse aggregate was 10 mm, with a specific gravity of 2.62. The constituents of the selected SCC mixes are given in Table 2. To improve flowability of the SCC mixtures, (SP) designed for the production of SCC (Glenium 51) with relative density of 1.1 at 20°C was incorporated in all mixtures shown in Table 3. The dosages of SP was modified to maintain a slump flow of 600 - 750 mm, T_{50} (4 to 10) sec., L-box index (>0. 75) (3 Ø10 mm with 50 mm gaps) and V-funnel flow (3 to 25) sec.

4. Preparation of Acid Solution

All concrete specimens were cured in water for 28 days, after which they were immersed in acid solution. The initial pH (2.3) of the solution increased quickly A digital portable pH meter was used for monitoring the pH levels of the sulfuric acid solutions. Specimens were fully immersed for 41 weeks.

Table 2: The constituents of the selected SCC mixes

Mix notation	Mix No.	C	SF	AT	Ch	Gu	SP
RSCC	M1	500	-	-	-	-	7. 0
SCCG	M2	350	-	-	-	150	3. 0
SCCLP	M3	350	-	-	150	-	7. 3
SCCLPAT	M4	315	-	35	150	-	9. 3
SCCLPSF	M5	315	35	-	150	-	8. 7

Note: for all mixes: water = 170l/m^3, sand =778 kg/m^3, gravel = 890 kg/m^3

Table 3: Properties of fresh concrete mixtures

Mix notation	Slump flow mm	T_{50} Sec.	L-box	V-funnel Sec.	Sp % wt. of cement per m^3
RSCC	720	6	1	17	7. 0
SCCG	650	5	1	18	3
SCC LP	620	9. 52	1	13	7. 3
SCC LPAT	700	5. 3	1	16	9. 3
SCCLPSF	680	7. 3	1	12	8. 7

Limitation for SCC

Slump depression (mm)	T_{50}, sec	L-box Index	V-funnel, sec
* 600-700	*2-5	* > 0. 8	*6-12
** 640-800	**4-10	** > 0. 75	**3-25

* *EFNARC* [14], ** The European Guidelines for SCC [15]

5. Hardened Concrete Properties

I. Compressive strength of concrete specimens before and after sulfuric acid attack

Table 4 and Figure 1 present the result of compressive strength of concrete cubes after 90, 182 and 289 days immersion in sulfuric acid solution. From Figure 1, the relative change of compressive strength after 289 was (80, 47, 25. 9, 67. 2 and 36) % compressive strength loss for M1, M2, M3, M4 and M5 respectively, it was observed that M1 (with high cement content) has a significant loss of strength, the reason for this anomaly is probably largely due to the fact that volume fraction of cement for concrete made with cement only was higher than that for concrete made with cement and other admixtures, since the acid attack cement only, the rate of loss in compressive with higher cement content was grater. For M4, (with HRA) the percentage loss of compressive strength was also high, comparable with other mixes without HRA , this may be attributed to the increases in the percentage of Al_2O_3 in HRA, and this may cause further reaction and corrosion of concrete that is exposed to sulfuric acid solution. This finding is also confirmed by Daczko *et al.* cited by Joorabchian [7], in his work he used HRM instead of HRA. Mixes with limestone powder (chalk powder) (M3), had the lowest compressive strength loss due to the high neutralization capacity and slower rate of reaction with acid relative to the filler. The better resistance of cements with limestone replacement to acid attacks can be attributed to four important factors: (i) the higher fineness of chalk powder effects positively on the resisting of SCC to acid solution. It filled the micro pores in cement paste and the ability of mortar to resist sulfuric acids attack was improved by the reduced permeability and porosity (ii) the existence of a high calcium carbonate (CaCO3) (68. 73 %) content increased the capacity of limestone powder to consume more aggressive acid, and (iii) the decreased proportion of cement reduced the portlandite (C–H) content (iiii) in the case of *sulfuric* acid attack, the calcium salt (gypsum) formed has very low solubility in water (0. 22 g/100 g water at 20 °C), a dense layer of gypsum was formed, which was capable of retarding the deterioration process by acting as a surface sealing layer [8].

In concretes with silica fume,(M5) has a higher compressive loss comparable with M3 (without silica fume) this may be attributed to the reduce in Portlandite available for reaction with the acid

$$C_3S_2H_3+H_2SO_4 \rightarrow CaSO_4.2H_2O+C_2S_2H_2 \quad (1)$$

This finding is supported by other researchers [8]. In the case of mixes with limestone powder M2 (gubra) According to the results, due to the high fineness (2.48 m^2/g) of the filler the reaction with sulfuric acid may also accelerate the deterioration of SCC and increase the loss of strength [8].

Table 4: Compressive strengths of concrete mixes

Mix No.	Compressive strength 28 days before immersion MPa	Compressive strength after immersion MPa		
		90 days	182 days	289 days
M1	72. 0	21. 0	15. 4	13
M2	45. 5	32. 0	29. 5	24. 1
M3	45. 0	38. 0	34. 5	33. 4
M4	51. 0	26. 0	20. 0	16. 8
M5	69. 0	41. 5	53. 0	44. 1

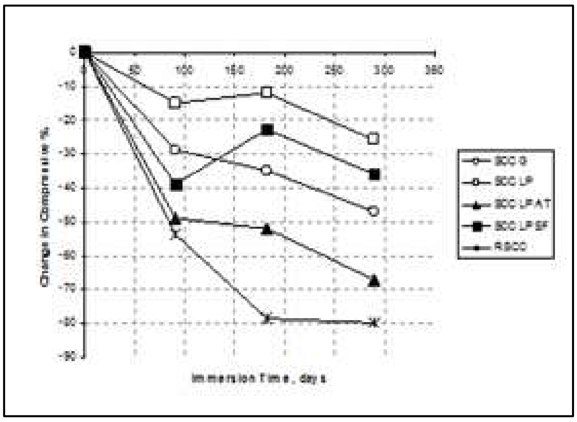

Figure 1: The relative change of compressive strength after immersion in H_2SO_4 solution

II. Mass loss of specimens of concrete specimens before and after sulfuric acid attack

Table 5 presents the results of density at 28 days for each concrete as well as the density of concrete cubes after 90, 182 and 289 days immersion in sulfuric solution. After immersion in H_2SO_4 solution, the relative change of mass was 18, 1.85, 2.7, 6.9, 11.76 % mass loss for M1, M2, M3, M4, and M5 respectively as shown in Figure 2. It was observed that at the age of 90 days some specimens exhibit loss of mass as shown in M3, while in mixes M1,M2,M4 and M5 there was an increase in concrete mass. The mass loss at this stage probably due to the micro cracks occurs between the matrix content after the diffusion of sulfuric acid. The mass gain can be attributed to saturation of the specimens or that is, in the initial conditioning age, the porosity in the concrete decreases which results in the mass increase, shown in Figure 2. At the end of the test, concretes made with silica fume,*(*M5, and Mixes with high reactive Attapulguite, these mixes have a higher mass loss comparable -with M3 (without Pozzolanic material) This finding is supported by other researchers [8, 9].

III. Splitting tensile strengths of concrete specimens before and after sulfuric acid attack (ft)

Table 6 shows the results of 28 day splitting tensile strength for all mixes as well as the splitting tensile strength of concrete specimen after 90, 182 and 289 days immersion in sulfuric acid solution. From Table 6 , The relative change of splitting tensile strength up to 289 days for M1, M2, M3, M4 and M5, was (63, 27, 41, 43 and, 41) % respectively as shown in Figure 3. It was observed at the age of 90 days all mixes exhibit loss of splitting tensile strength as shown in M1, M2, M3and M5, while in mixer M4 there was an increase in concrete tensile strength. The tensile strength loss at this stage is probably due to the micro cracks occur between the matrix content after the diffusion of sulfuric acid. The tensile strength gain can be attributed to saturation of the specimens or that is, in the initial conditioning age, the porosity in the concrete decreases which results in the tensile strength increase. As mentioned previously. With continued exposure, most of the specimens exhibit tensile strength loss, at the end of the test (282 days*)*, it was observed. Moreover, mix with silica fume M5 has the lowest resistance to sulfuric solution. I t can be inferred that the use of SF affects the (f_{cu}) in the same manner as (f_t).

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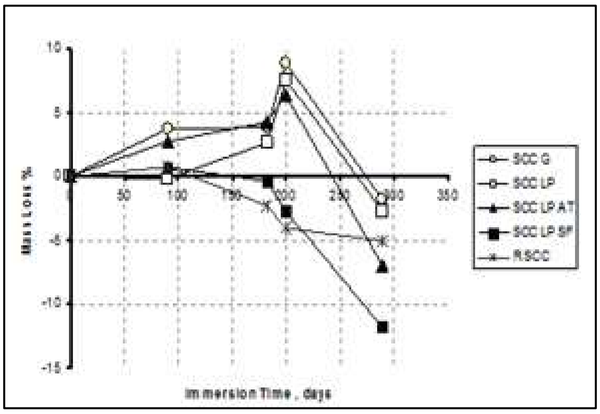

Figure 2: The relative change of density after immersion in H_2SO_4 solution

Table5: Density of concrete mixes

Mix NO.	Density of concrete specimens 28 days before immersion (kg/m^3)	Density of concrete specimens after immersion (kg / m^3)			
		90 days	182 days		289 days
M1	2577	2595	2518	2510	2450
M2	2519	2615	2528	2743	2473
M3	2534	2530	2600	2726	2465
M4	2482	2550	2520	2640	2310
M5	2516	2535	2505	2448	2220

Table 6: Splitting tensile strength of concrete mixes

Mix no.	Splitting tensile strength at 28-day before immersion (MPa)	Splitting tensile strength after immersion (MPa)		
		90 days	182 days	289 days
M1	3.8	3.5	2.4	1.4
M2	2.6	2.5	2.3	1.9
M3	2.7	2.1	1.9	1.6
M4	2.8	2.1	3.0	1.6
M5	5.0	3.6	3.9	2.0

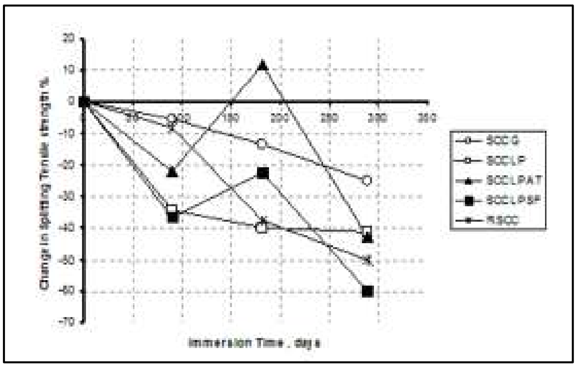

Figure 3: The relative change of splitting tensile strength after immersion in H_2SO_4 solution

IV. Modulus of Rupture of concrete specimens before and after sulfuric acid attack (fr)

Table 7 shows the results of 28 day modulus of rupture for all mixes as well as the modulus of rupture of concrete specimen after 90, 182 and 289 days immersion in sulfuric acid solution. The relative change of modulus of rupture at 289 days comparable with result of 28 day modulus of rupture, was (57, 27, 14, 33 and 41,) % loss for M1, M2, M3, M4 and M5 respectively as shown in Figure 4. After 90and 182 days immersion in sulfuric acid solution some specimens exhibit decrease or increase in modulus of rupture, as previously explained. The decreases in modulus of rupture probably due to the micro cracks occur between the matrix content after the diffusion of sulfuric acid. The increases in modulus of rupture can be attributed to saturation of the specimens or reduce in porosity due to the chemical reaction between the sulfuric acid and the paste which results increasing the modulus of rupture. Finely, most of the specimens exhibit loss in modulus of rupture, at the end of the test (282 days), it was observed that the use of SF affects the (f_r) in the same manner as (f_{cu}) and (f_t).

Table7: Modulus of rupture of concrete mixes

Mix no.	Modulus of rupture at 28-day before immersion (MPa)	Modulus of rupture after immersion (MPa)		
		90 days	182 days	289 days
M1	9.4	12.5	4.5	4.0
M2	5.5	6.0	4.5	4.0

M3	5.9	6.0	7.5	5.0
M4	6.0	4.0	5.0	4.0
M5	6.8	12.5	4.5	4.0

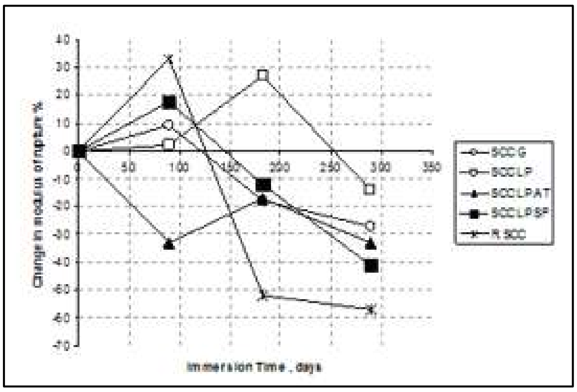

Figure4: The relative change of modulus of rupture after immersion in H_2SO_4 solution

6. Conclusions

At the present work the following conclusions were obtained:

1) SCC concrete mixes were susceptible to sulfuric acid attacks but differed in the level of deterioration depending on the type of concrete mixes

2) It was noticed that RSCC (with high cement content) has the highest strength loss 80 % comparable with mixtures containing different mineral admixtures

3) In concretes with silica fume (SCC-LP SF) has a higher compressive loss, the reduction was (36)% comparable with M3 (without silica fume) the reduction was 25.9 in addition for SCC-LP AT, (with HRA) the percentage loss of compressive strength was also high, comparable with other mixes without HRA (SCC LP) the reduction was 67.2 %.

4) Mixes with limestone powder (chalk powder) (SCC LP) , had the lowest compressive strength loss due to the high neutralization capacity and slower rate of reaction with acid relative to the filler the reduction was 25.9% on the other hand mixes with (gubra) (SCC-G) have higher compressive loss 47 %.

5) Concretes made with silica fume, (SCC-LP SF) and Mixes with high reactive Attapulguite (SCC LP AT), these mixes have a higher mass loss comparable with SCC-G and SCC-LP (without Pozzolanic material) the reduction was (11.76 and 6.9)% respectively and for mixes without Pozzolana material the reduction was (1.85, 2.7)%.

6) It was observed that the use of SF and HRA affects the modulus of rupture in the same manner as compressive and splitting tensile strength.

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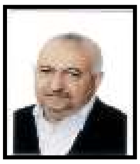

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