Microstructural investigation on fiber reinforced SCC subjected to sulphuric acid attack

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Abstract. All self-compacting concrete mixes are increasingly being used in many applications, some of which are subject to acid attack. This work aims to investigate the resistance of a variable range of SCC to sulphuric acid attack. The main studied variables include the cementitious materials type (silica fume and highly reactive Attapulguite), limestone powder (chalk powder and Al-gubra) and the inclusion of hybrid fibers (steel, plastic and polypropylene fibers). The powder content of the mixes was kept constant (500) kg/m³. The slump flow, L-box, and V-funnel were performed for mixes in their fresh state. In the present work, the specimens were immersed in sulphuric acid solution at concentration of (0.5%) upto 289 days after normal curing for 28 days. After the concrete hardened, two types of test were performed before and after immersing in sulphuric acid solution, viz. compressive strength and microstructure tests. The results obtained from this work, showed that concrete mixes with pozzolana materials only suffered high deterioration in mechanical properties as compared to concrete mixes with chalk powder only after exposure to 289 days in sulphuric acid solution in addition to, by using Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS), a number of elements were formed, which were indicated the product of hydration of cement paste before chemical immersed as measured with EDS equipment, as well as hand after chemical immersed, an increase in sulphur and calcium content of test sample, as measured with EDS equipped which confirms the identification of gypsum formation.

1. Introduction

The Deterioration of Concrete and mortar can be affected by different attacks under environmental water conditions. There are different kinds of environmental water attack, among which the acid attack is the most common. Thus, the microscopic structure deteriorates, moreover the strength of the structure decreases, and the structures finally get destroyed [1]

Different studies about the assessment of the deterioration of SCC subjected to sulphuric acid using microstructure technique have been completed. Attiogbe and Rizkalla [2] studied the microstructure degradation using SEM / EDS tests. Different concrete mixtures (Ordinary Portland Cement type I and type V) were immersed in 1% sulphuric acid solution for 10 weeks. A change in sulphur content of the test samples was used as the chemical indicator of the degree of deterioration. They suggested that the samples submit expand the size as a result of the sulphuric acid attack. A comparison between SEM photo for un attacked and attacked samples shows that the acid reacts with the cement leading to the formation of more porous material. In their study the EDS analysis showed that the sulphur content of the acid-attacked specimen is higher than that of the un attacked specimen.
Senhadji et al. [3] used SEM and EDS analysis to study the microstructure changes in cement paste. SEM photo, shows the precipitation of (gypsum), (needle-like crystals) in the surface cracks. They reported that, the formation of gypsum results in the degradation of mortar. EDS test showed elements such as sulphur, oxygen, and calcium, indicating the determination of gypsum formation.

Siad et al. [4] represented a study on the mechanism of deterioration of different types of concrete by using SEM and EDX analysis. The immersion period of all concrete specimens in acid solution was about 12 weeks. The SEM and EDAX data obviously showed that both calcium and sulphur were the dominant elements. Kim and Lee [5] used SEM and EDS, microstructural test to examine concrete element of concrete structure subjected to sewage water for nearly ten years. In this study specimens were taken from a sewage treatment tank. The SEM and EDS show the presence of sulphate products due to H2SO4 attack. The SEM of the samples, which was taken from the surface of the samples indicates the existence of a large amount of gypsum. They reported that formation gypsum is one of the causes of low compressive strength of the concrete. Yingfang and Haiyang [6] examined the pore characteristics of the concrete by (SEM) and (EDS) analysis. They used acid solution with different pH levels ranging from 1.0 to 2.5. From the SEM images, they observed that gradual changes occur in the microstructure of concrete samples. They reported that, with the constant exposure, the C–S–H becomes denser, more the C–H crystal takes shape, the internal micro cracks become wider.

The aim of this research is to study the deterioration of SCC subjected to sulphuric acid using microstructure technique and to study the correlation between the durability problem and the microstructure.

2. Materials
Portland cement (PC), (ASTM C150 – Type) [7] was used as a binder. The cement conforms to the Iraqi standardwas [8], silica fume of class N pozzolans [9], high reactivity Attapulguite (HRA) to ASTM 618-03[10]. 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 [11]. Two types of limestone powder (Gabra and chalk powder) were used throughout this investigation. Table (1) illustrates the properties of the materials [12]. Three types of fibers were used for the purpose of this study. These types are steel, plastic and polypropylene fibers. The researchers used volume of fibers in order to obtain the suitable workability. Table (2) and figure (1) show the properties and the photos of the fibers. Table (3) illustrates the SCC mixes. The fresh properties of the binder conformed to rules guiding for SCC design [13] [14]. The results of fresh properties of SCC mixtures are summarized in Table (4).

Table 1. The properties of the materials [12]

| Oxides   | Cement | HRA  | Silica fume | Gabra | Chalk powder |
|----------|--------|------|-------------|-------|--------------|
| SiO2     | 20     | 47.91| 96.7        | 1.50  | 2.24         |
| FeO3     | 3.9    | 1.81 | 0.07        | 0.08  | 0.12         |
| Al2O3    | 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         |
| SO3      | 2.03   | 1.81 | 0.61        | <0.07 | <0.07        |
| Specific gravity | 3.2 | 2.4 | 2.13 | 0.774 | 3.17 |
| Fineness m²/g | 4.37 | 2.1 | 157 | 2.48 | 3.17 |
Table 2. The properties of fiber

| Types of fiber | Plastic | Polypropylene | Micro steel |
|----------------|---------|---------------|-------------|
| Description    | crimped | monofilament  | straight    |
| Length of fiber (mm) | 30      | 12            | 15          |
| Tensile strength (MPa) | 250-300 | 350           | 2600        |
| Aspect Ratio    | 63      | 66.7          | 75          |
| Specific gravity (g/cm³) | 1.14    | 0.91          | -           |

Figure 1. The photos of the fibers

(a) Plastic fibers  (b) Micro steel  (c) Polypropylene fibers

Table 3. The SCC mixes

| Mix proportion | Mix notation | cement | SF | AT | CH | Gu | Sp | Hybrid fiber by volume |
|----------------|--------------|--------|----|----|----|----|----|------------------------|
|                |              |        |    |    |    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |
| SCC LP         | M1           | 350    | 150|    |    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |
| SCC G          | M2           | 350    | 150| 3  |    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |
| SCC LP AT      | M3           | 315    | 35 | 150|    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |
| SCC LP SF      | M4           | 315    | 35 | 150|    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |
| SCC LP SF HR1  | M5           | 315    | 35 | 150|    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |
| SCC LP SF HR2  | M6           | 315    | 35 | 150|    |    |    | Plastic (PL) Polypropylene (PP) Micro steel |

Note 1: water, sand and gravel are 170 l/m³, 778 kg/m³ and 890 kg/m³ respectively
Note 2: SF = silica fume, AT = high reactivity Attapulguite, CH = Chalk powder, Gu = Gubra, SP = superplastizicer

Table 4. The fresh properties of SCC mixtures

| Mix proportion | Slump depression mm | T50 Sec. | L-box index | V-funnel Sec. | Sp % wt. of cement per m³ |
|----------------|---------------------|----------|-------------|---------------|----------------------------|
Acid solution
The pH of the solution was about (2.3). The Specimens were immersed for 289 days after curing in water for 28 days.

3. Hardened concrete properties

3.1. Crushing strength of concrete
Table (5) shows the results of crushing strength. The target value was 45 Mpa. From figure 1, the change of strength after 289 days was (26, 47, 67, 36, 63 and 47) % of compressive strength loss for (M1, M2, M3, M4, M5 and M6) respectively comparable with corresponding mixes cured at 28 days. For SCC LP AT, (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 deterioration and further reaction of concrete that is exposed to sulfuric solution. This finding is also confirmed by Daczko et al. cited by Joorabchian [15], (in their work they used high reactive mitekaolin instead of AT). 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 resistance of mixes with limestone powder to acid attacks can be attributed to two important factors: [15]
1. The high percentage of (CaCO_3) (68.73 %) content increased the ability of limestone powder to consume more aggressive acid, and decreased the portlandite (C–H) content which was formed by the cement.
2. Gypsum can act as a surface sealing layer which can retard the deterioration process of the acid

Table 5. Compressive strengths of concrete mixes

| Mix notation | Mix No. | Crushing strength 28 days before immersion (Mpa) | Crushing strength after immersion (MPa) | Reduction of strength after immersion % |
|--------------|---------|--------------------------------------------------|----------------------------------------|------------------------------------------|
| SCC LP       | M1      | 69.0                                             | 41.5                                   | 26                                       |
| SCC G        | M2      | 45.5                                             | 32.0                                   | 47                                       |
| SCC LP AT    | M3      | 51.0                                             | 26.0                                   | 67                                       |
| SCC LP SF    | M4      | 69.0                                             | 41.5                                   | 36                                       |
| SCC LP SF HR1| M5      | 68.5                                             | 30.0                                   | 63                                       |
| SCC LP SF HR2| M6      | 67.5                                             | 45.0                                   | 47                                       |

Concretes with silica fume and hybrid fibers, (M5 and M6) have a high compressive loss as shown in Fig (2) comparable with M1(without silica fume). This may be attributed to the reduction in portlandite available for reaction with the acid, because it has already reacted with the SF, producing
C–S–H and reducing the cement paste’s permeability at the same time. Thus, acid attack is consequently limited to the surface and also acid solution attack to C–S–H in transition zone according to decalcification reaction.

\[
\text{CaSiO}_2 + 2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{Si(OH)}_4 + \text{H}_2\text{O} \quad \ldots \ldots (1)
\]

This finding is supported by other researchers [16].

There is another reason about the negative impact of silica fume, which can be clarified as follows. Inspite of densification of the pore structure of SCC by silica fume in order to achieve lower permeability; low resistance to acid attack has been established. This is due to the negative effect of poor densification creating less space to accommodate stresses caused by the growth of large gypsum crystals. This finding is also supported by other researchers [17] [18].

![Figure 2](image_url)

**Figure 2.** The percentage change in crashing strength after immersion in H\(_2\)SO\(_4\) solution

3.2. *SEM and EDS for SCC Concrete Samples*

(SEM) and EDS were carried out to identify the products formed before and after H\(_2\)SO\(_4\) solution attack. The results are exhibited in figures (3) to (14), for M1, M2, M3, M4, M5, and M6, respectively.

In the present study, sulfur and calcium component percentage from the EDS are of primary interest. This is because both of these elements are also formed as a result of the reaction between sulfuric acid and cement paste. This finding is observed by another researcher [2].

From the SEM photos and EDS analyses before attack, the following was observed:

1. A dense structure was formed for all samples before acid immersion, as shown from SEM photos, also the presence of void in some parts of samples with hybrid fibers as shown in figures (7) A and (7) B.
2. From EDS, different elements were formed such as Ca, O, Al, Si, C, Mg and S as a result from the hydration product.

After immersing in H\(_2\)SO\(_4\) for 289 days, the following was noticed:

1. The EDS data clearly indicated that the dominant elements was calcium, sulfur and gypsum. This is agreed with observations by different researchers [4] [5].
2. The micrograph of concrete samples exposed to H\(_2\)SO\(_4\) for 289 days indicated that these samples submit significant deterioration because it is highly porous as shown in SEM micrograph, as can be seen from a comparison of the SEM images before and after exposure to H\(_2\)SO\(_4\) solution.
3. Some chemical reaction was participated one fiber as shown in figure. (11), which can reduce the bond between the cement matrix and the fibers and resulted in more porous in cement matrix.
Figure 3. The Microstructure photo (SEM and EDS) of un attacked SCCLP AT sample

Figure 4. The Microstructure photo (SEM and EDS) of un attacked SCCLP SF sample

Figure 5. The Microstructure photo (SEM and EDS) of un attacked SCC LP sample

Figure 6. The Microstructure photo (SEM and EDS) of un attacked SCC G sample
Figure 7. The Microstructure photo (SEM and EDS) of un attacked SCC LP HR1 sample

Figure 8. The Microstructure photo (SEM and EDS) of un attacked SCC LP HR2 sample

Figure 9. The Microstructure photo (SEM and EDS) of attacked SCC LP SF HR2 sample

Figure 10. The Microstructure photo (SEM and EDS) of attacked SCC LP AT sample
Figure 11. The Microstructure photo (SEM and EDS) of attacked SCC LP SF HR1 sample

Figure 12. The Microstructure photo (SEM and EDS) of attacked SCC LP SF sample

Figure 13. The Microstructure photo (SEM and EDS) of attacked SCC G sample
4. Conclusion

1. Concretes with silica fume, (M4, M5 and M6) gave high compressive strength loss after exposure to acid solution for 289 days. The reduction was (36, 63 and 47) % respectively comparable with M1 (without silica fume). The reduction in compressive strength was 26%. For M3, (with AT) the percentage loss of compressive strength was also high as compared to other mixes without AT; the reduction was 67%.

2. Mixes with limestone powder (chalk powder) (M1) had the lowest compressive strength loss after 289 days exposure to acid solution; the reduction was 26%. On the other hand, mixes with (Algubra) (M2) gave a higher compressive strength loss (47) % comparable with mixes (M1).

3. The mixes containing is not clining mixture of plastic and micro steel fibers were better than the others mixes in terms of the compressive strength.

Depending on the microstructure results, the following observations can be concluded:

1. After immersion of specimens in sulfuric acid solution, the increase in sulfur and calcium content of test sample, as measured with EDS equipment, which shows the identification of gypsum formation, is a good sign to the extent of damage in concrete because of exposure to sulfuric acid.

2. The micrograph from SEM test of concrete samples immersed in H₂SO₄ for 289 days indicated that these concrete samples showed significant deterioration because it is highly porous, as can be seen from a comparison of the SEM images before and after exposure to H₂SO₄ solution.

References

[1] S Liu, L Li, Z Wang, J Wang and M Rao 2012 Study on Strength and Microstructure of Cement Pastes Containing Limestone Powder under Flowing Acid Solution Condition International Scholarly Research Network (ISRN) Ceramics, pp 1-6

[2] E K Attiogbe and S H Rizkalla 1988 Response of concrete to sulfuric acid attack. ACI Materials Journal I November-December, pp 481-488

[3] Y Senhadji, G Escadeillas, M Mouli, H Khelafi and Benosman 2014 Influence of natural pozzolan, silica fume and limestone fine on strength, acid resistance and microstructure of mortar Powder Technology Vol. 254, pp 314–323

[4] H Siad, H A Mesbah and S K Bernard 2010 Influence of natural Pozzolan on the behaviour of self-compacting concrete under sulphuric and hydrochloric acid attacks, comparative study The Arabian Journal for Science and Engineering, Vol. 35, pp 183-195

[5] S S Kim and S T Lee 2010 Microstructural observation on the deterioration of concrete structure for sewage water treatment KSCE Journal of Civil Engineering, Vol. 14, pp 753-758

[6] F Yingfang and L Haiyang 2013 Pore structure in concrete exposed to acid deposit Construction and Building Materials, Vol.49, pp 407–416
[7] ASTM C150, 2002 Specification for Portland Cement Annual Book of ASTM Standard, Vol. 04-02
[8] Iraqi Specification, No.5., 1984 "Portland cement"
[9] ASTM C1240- 03, 2003 Standard Specification For The Use Of Silica Fume As A Mineral Admixture In Hydraulic Cement Concrete , Mortar And Grout, Vol. 4.2, p.6
[10] ASTM C618-03, “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete”, Annual Book of ASTM Standard, Vol. 04-02, February, p. 3.
[11] S H M Al-Amide, 2012 Some properties of concrete containing fired local attapulgite clay MSc. Thesis, University of Technology
[12] Zghair L A, Frayyeh Q J & Salman M M 2017 Performance of self-compacting concrete containing Pozzolanic materials in aggressive environment. Engineering and Technology Journal, 35(5Part (A) Engineering), pp 439-444
[13] EFNARC, 2002 Specification and Guidelines for Self-Compacting Concrete February 2002, p 32
[14] Self-compacting concrete European project group 2005 The European Guidelines for Self-Compacting Concrete” May, pp 43-56
[15] S M Joorabchian 2010 Durability of concrete exposed to sulfuric acid attack. Thesis, Ryerson University, Canada, pp 1-116
[16] Y Senhadji, G Escadeillas, M Mouli, H Khelafi and Benosman 2014 Influence of natural pozzolan, Silica Fume And limestone fine on strength, acid resistance and microstructure of mortar Powder Technology Vol. 254, pp 314–323
[17] S Turkel, B Felekoglu and S Dulluc 2007 Influence of various acids on the physico–mechanical properties of pozzolanic cement mortars Dokuz Eylul University India, Vol. 32, Part 6, December, pp 683–691
[18] C Özlem, E Jan, F Dimitri, H Gert, V Lucie, V G Dionys, D Bram, V John and S Geert 2011 Microstructural Changes In Self-Compacting Concrete By Sulphuric Acid Attack Chemistry of Cement, p 436