COMPARATIVE STUDY BETWEEN MICROSTRUCTURE OF A NOVEL DURABLE CONCRETE AND NORMAL CONCRETE SUBJECTED TO HARSH ENVIRONMENTS

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Abstract: Degradation of concrete members exposed to aggressive sulphuric acid environments is a key durability issue that affects the life cycle performance and maintenance costs of vital civil infrastructures [1]. Groundwater, chemical waste, sulphur bearing compounds in backfill, acid rain in industrial zones and biogenic acid in sewage systems are the main sources of sulphuric acid affecting concrete structures. In this research, microstructures of a novel acid resistant concrete (ARC) and a type of conventional concrete (CC), as the reference, have been studied in the laboratory subjected to accelerated testing. For this purpose, ARC and CC, were immersed in 7% (by volume) sulphuric acid solution. Mechanical properties of both concretes as well as their microstructures were examined after 28 days of curing and then after two, four and eight weeks of exposure to acid. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and X-ray mapping (XRM) were employed to analyse the microstructure of concretes before and after exposure to acidic environment. The results of this analysis revealed interesting facts about the mechanism of sulphur penetration in both concrete samples. In addition, they showed differences in the crack locations and propagation patterns and in interfacial transition zones (ITZ) of concretes, particularly after acid exposure. These changes of microstructures, as was proved in experimental tests, could significantly contribute to changing the ductility of the concretes in modulus of rupture (MOR) test.

# 1 INTRODUCTION AND BACKGROUND

The chemistry of hydration products, pore structure and mechanical properties of hardened concrete are significantly affected by the environmental conditions to which the concrete is exposed during its service life [2]. Sulphuric acid in groundwater, chemical waste [3] or generated from the oxidation of sulphur bearing compounds such as pyrite in backfill [4], acid rain of which sulphuric acid is a chief component [3] and biogenic sulphuric acid in sewage systems can attack substructure concrete members and impose considerable damage by corrosion [5].

When concrete is exposed to sulphuric acid three main chemical reactions occur as follows;

- Gypsum formation resulting from conversion of the calcium hydroxide $Ca(OH)_2$ to calcium sulphate $(CaSO_4)$ as per the following reaction [6].

$$CH + H_2SO_4(aq) \rightarrow CaSO_4 \cdot 2H_2O(s) \qquad (1)$$
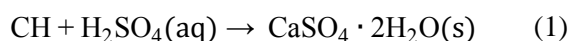
- Ettringite formation which is due to conversion of hydrated calcium aluminate to calcium sulpho aluminate $(3CaO.Al_2O_3.3CaSO_4 \cdot 32H_2O)$ as shown in the following equation [1];

$$3CaO.Al_2O_3.12H_2O(s) + 3(CaSO_4 \cdot 2H_2O)(s)$$
$$+ 14H_2O(l) \rightarrow 3CaO.Al_2O_3.3CaSO_4 \cdot 32H_2O$$

$$(2)$$
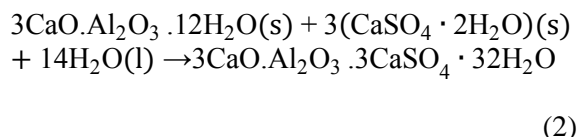
- Decalcification – decomposition of the hydrated calcium silicates (C-S-H), which is responsible for provision of the strength in concrete according to the below reaction [6].

$$C_3S_2H_3 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$$
$$+ C_2S_2H_2 \qquad (3)$$
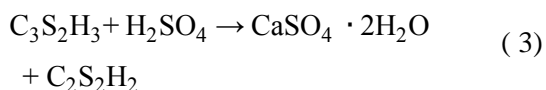
These chemical reactions lead to expansion, cracking [6, 7], and loss of strength and elastic properties of concrete [6, 8-10]. Santhanam, Cohen [11] mentioned that both ettringite and gypsum have expansive and destructive character, while others such as Schmidt, Lothenbach [12] stated that the contribution of gypsum is limited while the expansion of ettringite dominates.

Many research studies have examined the microstructure of cementitious materials subjected to sulphuric acid [13-19] . The main focus of the microstructural analysis in these studies has been on the formation of gypsum and/or ettringite in different areas and crack and micro crack formation and their patterns as it can explain changes of mechanical and structural properties of concrete.

Numerous research works have aimed to enhance the acid resistance of different concretes by use of sulphate resistant (SR) cements, supplementary cementitious materials (SCMs), varying the w/c ratio and aggregates and development of polymer and geopolymer concretes. However, to date, there is no standardised concrete for structural applications in acidic environments where the pH< 4 and in such environments construction has to be avoided, or old fashioned protective precautions such as coating should be applied which have the potential for high cost for repair and maintenance.

In this research, a novel acid resistant concrete was developed and evaluated in the laboratory. This was carried out under an accelerated acidic environment and its mechanical, structural and microstructural properties have been expansively investigated after different periods of exposure to sulphuric acid. The main findings from the mechanical and structural properties tests have been discussed in previous publications [20, 21] and the scope of the current paper was to examine the microstructures of this new concrete (ARC) and conventional concrete (CC) and investigation of the effect of changes of microstructure on results of MOR tests after exposure to acid.

2 EXPERIMENTS

2.1 Materials

2.1.1. Conventional Concrete (CC)

Conventional concrete (CC) was supplied by Concrite Pty Ltd, NSW Australia. It had

28-day compressive strength of 40 MPa with the water to binder ratio of 0.4. The CC mix included 350 kg/m^3 cement, 150 kg/m^3 fly ash, 960 kg/m^3 coarse and 661 kg/m^3 fine aggregates plus 2.3 litre/m^3 water reducing admixtures (under commercial name of Pozz 80 from BASF the Chemical Company). The cement and fly ash used in CC were shrinkage limited Portland cement and low calcium fly ash (type F). The coarse aggregates had maximum size of 10 mm and were sourced from Dunmore Quarry, NSW, Australia and fine aggregates included 600 kg/m^3 of Nepean river sand and 150 kg/m^3 of Kurnell sand. The target slump of the concrete was 140 ± 10 mm and it had the mass per unit volume and air content of 2,360 kg/m^3 and 1.0 % respectively.

2.1.2. Acid Resistant Concrete (ARC)

The newly developed acid resistant concrete (ARC), was prepared in the laboratory. It consists of an acid resistant mortar (ARM) commercially available in Australia, coarse aggregate (similar to the CC) and same admixtures to control the workability and water to cement ratio. Its 28-day compressive strength was 31 MPa, the ratio of course to fine aggregate was 0.5, and water to binder ratio was 0.4. It had a slump of 140 ±10 mm and mass per unit volume and air content of 2,150 kg/m^3 and 0.8 %. ARM contains less than 10% Portland cement (Type GP), 10%-30% fly ash, 1%-10% silica fume, 30%-60% silica sand and about 10% silica and poly silicates, different types of fibres and some admixtures. The exact percentage and type of ARM ingredients are not revealed due to the confidentiality agreements with the manufacturer company.

To cast the ARC specimens, firstly, coarse aggregates and then a part (2/3) of required water were added to the mixer and mixing procedure commenced. Then, ARM composition was gently added to the mixer. Afterward, the rest of water including required water reducer was added and the composition was mixed for 5 minutes before casting. The entire procedure of casting, vibration, surfacing, finishing and curing was performed exactly similar to the CC.

2.2 Test procedure

2.2.1 Sample Preparation and Equipment

For modulus of rupture (MOR) test, 100 mm × 100 mm × 400 mm prisms were tested. To prepare samples for microstructural analysis, CC and ARC cylinders with the dimensions of 100 mm × 200 mm, were initially cured in lime water for 28 days and then immersed in acid solution. The acid solution was sulphuric acid solution with concentration of 7% (by volume) to perform an accelerated test. Figure 1 shows the immersion of specimens in acid containers. Concentration of the acid solution was monitored and adjusted weekly not to lose the exact concentration due to degradation of concrete samples in the solution and its neutralising effect as an alkaline material.

Figure 1 : Immersion of concrete specimens in 7% sulphuric acid solution.

Samples were taken out of acid containers after different periods of exposure (0 weeks, 2 weeks, 4 weeks and 8 weeks) to be examined. After taking the specimens out of acid solution, they were washed with water and a wire brush and their surfaces were dried with tissue. This procedure was applied carefully in order to be as consistent as possible for all specimens.

The MOR of ARC and CC were investigated after 28 days of lime water curing and then the specimens were immersed in 7% sulphuric acid solution and were tested at

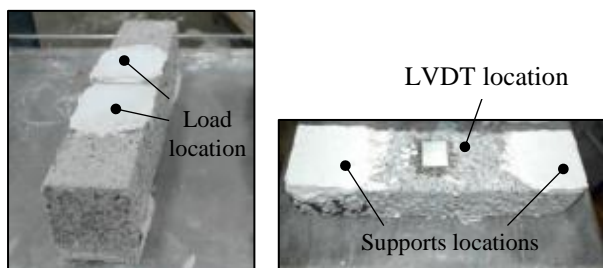different ages of exposure to acid after some preparation for CC specimens (Figure 2).

Figure 2 : Preparation of CC specimens after 4 weeks of exposure to 7% sulphuric acid solution.

To find the depth of penetration of acid in both types of specimens, a special indicator namely, Thymol blue (TB) was used (See Figure 3). For this purpose 100 mm × 200 mm cylinders were cut into four discs of 100 mm × 150 mm after different periods of acid exposure. They were then sprayed with a solution of Thymol blue. The acid affected and intact areas are shown (Figure 3) by yellow and blue zones, respectively. For microstructural analysis, small samples (20 mm × 20 mm × 20 mm) were cut from the cylinders used in TB test. Eight samples including four CC and four ARC from both acid exposed specimens and the specimens under curing (lime water), were cut from the external surface of the cylinders (shown by red boxes in Figure 3).
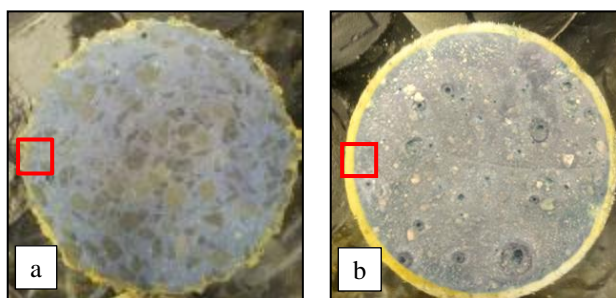

Figure 3 : Finding the depth of acid penetration in a) CC, b) ARC by use of Thymol blue indicator spraying.

Both non-polished fractured and polished samples were examined as each of them could provide valuable information about the mechanism of acid attack on both materials.

To prepare the former, the sample was simply cut from the sample and mounted for SEM and EDS investigations in a JEOL 6510LV SEM. For the latter one (polished sample), after cutting the sample, it was placed in a plastic mould and set in an epoxy resin. The sample was placed under vacuum for 24 hours to cure. Once the resin cured, the sample was ground on a rotary lapping machine using silicon carbide sand paper ranging from 80, 120, 240, 400, 600, and 1200 grit size for 30 mins and then further polished using 1µm and 3µm diamond paste on synthetic cloth discs. Samples after preparation were carbon coated (30 nm) (Figure 4).

Samples were X-ray mapped using a JEOL JXA-8600 super probe SEM with an Amptek EDS silicon drift detector utilising Moran Scientific acquisition software system [22].
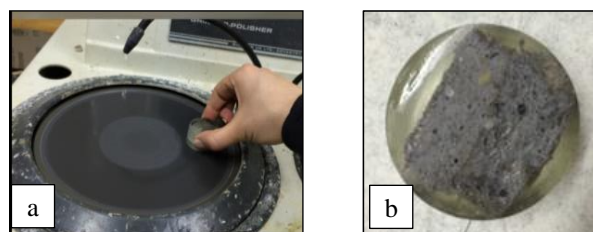

Figure 4 : Sample preparation for high vacuum machines, a) polishing the sample on rotary machine and sanding paper, b) polished sample.

2.2.2 Test method

In this research an accelerated test program was used to investigate the mechanism of acid attack on two different concretes. High vacuum and low vacuum SEM imaging with different magnifications and energy dispersive spectroscopy (EDS) were used to investigate the changes of microstructure (mainly microcracks formation) and chemical elements in CC and ARC after exposure to acid. X-ray diffraction (XRD) was employed to determine the phases found in acid treated layers of concrete samples and X-ray mapping (XRM) was used to find the distribution and associations of elements in samples interfaces after exposure to acid.

MOR tests were also performed according to Australian Standard AS1012.11 (2000) in which concrete prism is subjected to 4 - point

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flexural load at a loading rate of 1 ± 0.1 MPa/min until fracture.

3 TEST RESULTS AND DISCUSSION

## 3.1 Investigation of Microcracks

Concrete is generally full of micro-cracks. Upon loading, these micro-cracks propagate and their accumulation can lead to the development of major cracks and subsequently failure [23, 24]. These microcracks have been reported to have lengths of less than 0.1 mm [25], which exist in concrete even before applying any load. They are mostly located in interfacial transition zones (ITZ) of concrete and their number, size and propagation can affect different properties of concrete such as strength, ductility and durability.

In the SEM images of both CC and ARC pastes before exposure to acid some microcracks were observed. However, SEM observation of the acid exposed pastes proved development of more microcracks which resulted in cracks in some cases in the paste of CC and ARC. When interpreting microcracks in SEM images, it should be noted that some cracks could be the result of polishing or other stages of preparation. To address this issue, all samples, were prepared according to the same procedure. Secondly, and more importantly, EDS analysis and more careful SEM were utilised to make sure these cracks were the result of chemical reactions in the paste and not artefact [26] (by finding expansive products around the cracks).

For both types of concretes, microcracks are mostly observed to initiate from interfacial transition zones (ITZ) around the aggregate where the microcracks usually exist in concrete in normal situations and without any exposure to aggressive agents (See Figure 6). This is in agreement with the findings of previous researchers [23].
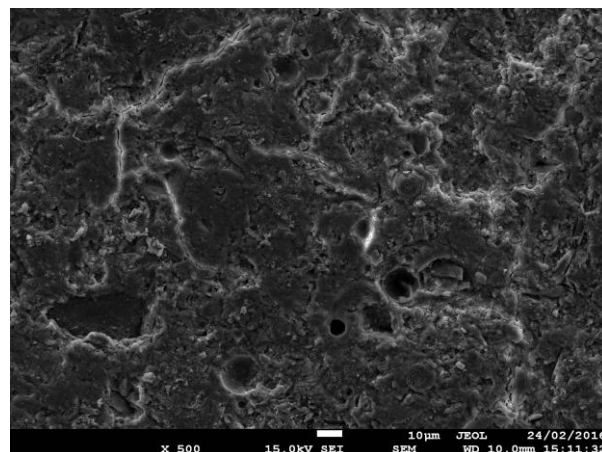
(a)
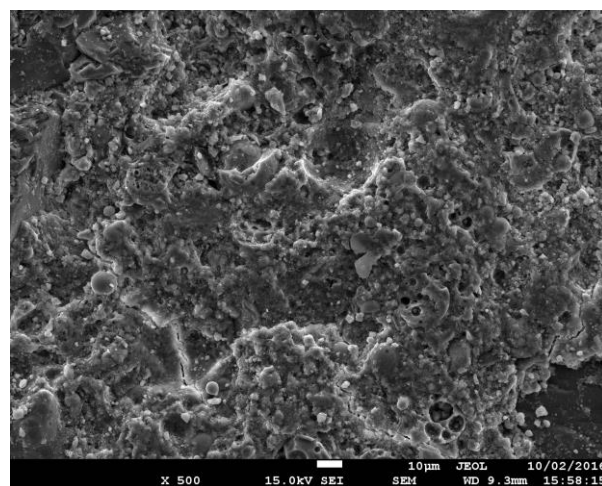
(b)

Figure 5 : SEM images, showing microcracks formation after 4 weeks of exposure to 7 % sulphuric acid a) CC and b) ARC samples.
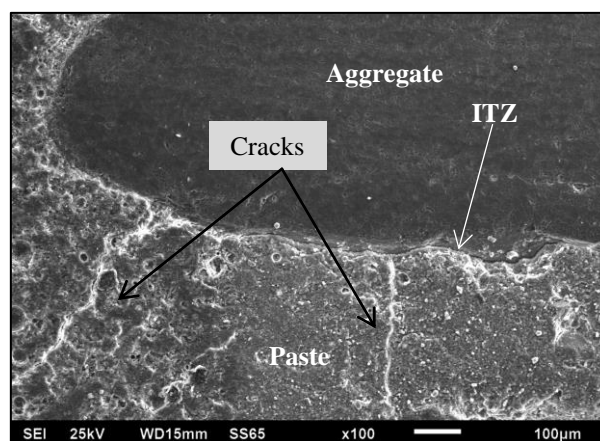

Figure 6 : SEM images, showing cracks initiating from the ITZ around the aggregate in CC.

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3.2 Flexural behaviour after acid exposure

Investigation of flexural behaviour of CC and ARC specimens after exposure to acid showed some increase in ductility for both types of concrete. This statement is based on the post-peak deflection in MOR test which is a measure of ductility. Figure 7 shows the load-mid span deflection of CC and ARC specimens after 28 days of water lime curing and then, different periods of immersion in 7% sulphuric acid. As shown, for both types of concretes more ductile behaviour is observed. As is well known, microcracks can control different properties of concrete, particularly its flexural behaviour. Development of microcracks in CC and ARC after acid exposure seems to be one of the reasons for higher ductility of acid exposed samples in modulus of rupture tests.
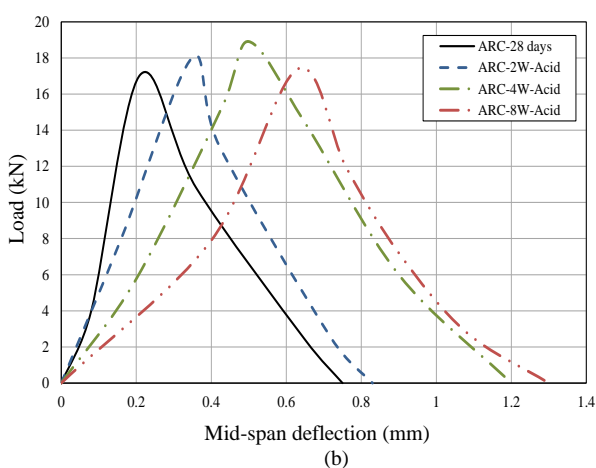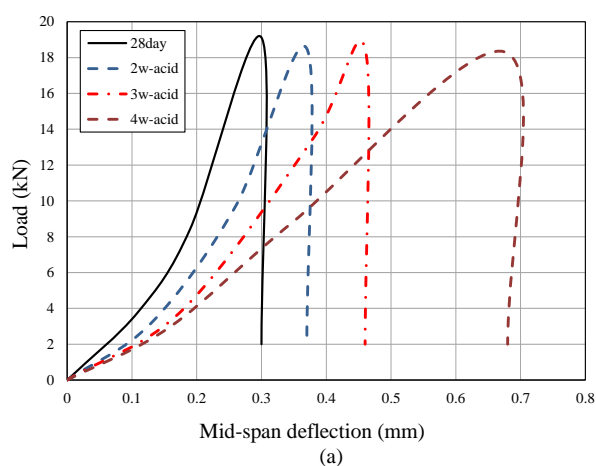

(a)

(b)

Figure 7 : Load-mid span deflection of a) CC, b) ARC specimens in modulus of rupture test (MOR) after different periods of exposure to 7% sulphuric acid.

In addition, SEM imaging of non-polished fractured surface of samples revealed the crack bridging role of existing fibres in ARC after exposure to acid (shown in Figure 8). They seem to contribute to propagation of cracks and maintaining the whole mix together in acid affected layer in the mix.
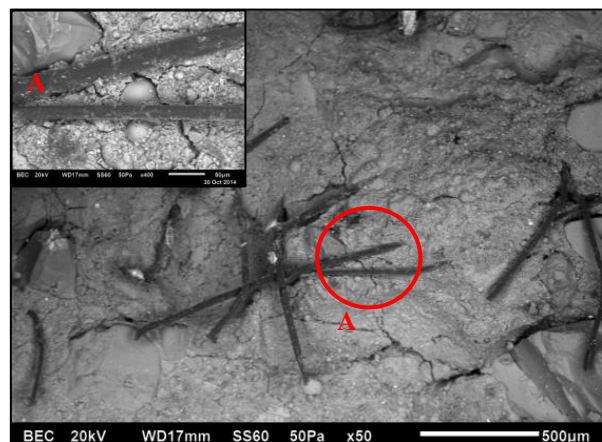

Figure 8 : SEM images of fibres bridging the cracks in ARC specimens after exposure of specimens to acid (magnification of ×50 and ×400).

3.3 Elements distribution after exposure to acid

The results of X-ray mapping (XRM) are shown in Figure 9 and present the distribution of calcium and silica elements in acid exposed CC and ARC specimens. In CC, almost the entire acid exposed layer has been degraded and washed out and sulphur could be found on a very small piece of the external layers of sample (Figure 9b) and in the rest of its paste there was no trace of sulphur. Calcium was observed in both bulk paste and acid affected layer.

In ARC, the acid exposed layer of the sample has not been degraded and is still there. However, X-ray mapping shows the penetration of sulphur element in this layer (Figure 9d). Given the existence of calcium in this layer for both CC and ARC, there was a potential for formation of gypsum that was further investigated by SEM, EDS and XRD analysis.
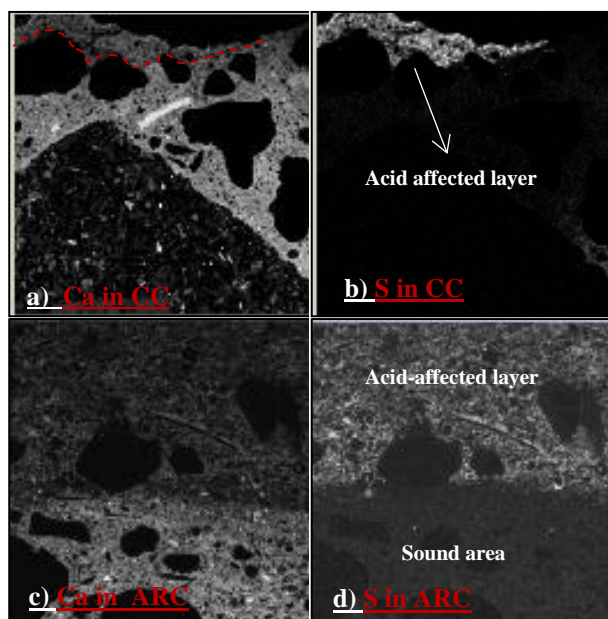
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Figure 9 : X-ray mapping of interface of samples showing the distribution of: a) Ca in CC, b) S in CC, c) Ca in ARC and d) S in ARC after 8 weeks exposure to 7% sulphuric acid.

3.4 Expansive products after acid exposure

The acid exposed layers of CC and ARC were examined by SEM imaging and EDS to find the new products such as gypsum or ettringite resulting from the chemical reactions between the sulphuric acid and cementitious materials. In acid affected layers of CC, no ettringite was observed. Microcracks were mostly formed in interfacial transition zone (ITZ) around the aggregates due to formation of gypsum in these areas. Formation of gypsum in ITZ could be attributed to high amount of calcium and existence of larger crystals of calcium hydroxide (CH) in this zone and their reaction with sulphuric acid. Figure 10 shows SEM images and EDS analysis of the formed gypsum around the ITZ which seems to be responsible for separation of aggregates in acid affected layers of CC by its expansive reaction. However, formation of gypsum does not seem to be the main reason for the high degradation of the external layers of CC as the existing gypsum crystals, consequent microcracks and cracks do not appear to be that destructive. According to previous research in this area and these observations, it is concluded that degradation of CC after acid exposure is mainly due to

decomposition of C-S-H or in other words, acidic effect of sulphuric acid rather than the effect of sulphur element.
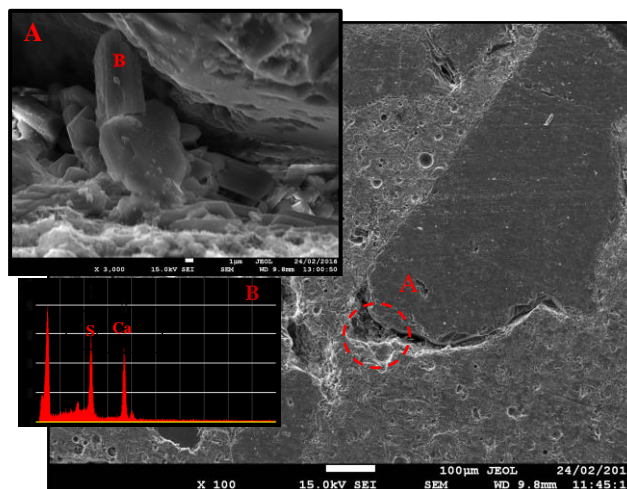

Figure 10 : SEM images, showing the formation of gypsum crystals in ITZ around the aggregates in CC after 4 weeks immersion in 7% sulphuric acid.

In acid affected layers of ARC, much less gypsum was captured compared to CC (Figure 11). This is attributed to less $Ca(OH)_2$ in ARC which is the most vulnerable phase in sulphuric acid attack. In addition, the crystals of gypsum are more dispersed in the mix and each time a single crystal of gypsum could be captured surrounded by different phases including mostly silica whereas in CC, gypsum crystals were found to be mostly in ITZ around the aggregate and they were not dispersed in the whole acid affected layer.
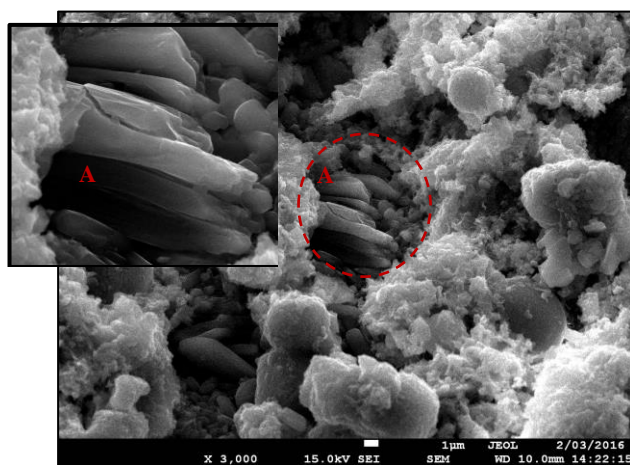

Figure 11 : SEM images, showing the formation of ettringite in the paste of ARC after four weeks of exposure to 7 % sulphuric acid.

With regarding to the ettringite, it should be mentioned that it is not stable in very acidic environments (pH less than 10.7) [27], hence, there is a hypothesis that maybe it used to be in acid affected layers of CC before degradation or in ARC at early ages of exposure to sulphuric acid but in any case it is not there after this period of acid exposure.

4 CONCLUSIONS

Sulphuric acid is an aggressive agent available in different environments and causes durability issues for concrete, mostly due to its chemical reactions with the hydration products of cement in concrete. This attack impacts the life cycle performance and maintenance cost of concrete members in different structures and leads to expansion, cracking and loss of main properties of concrete.

Despite numerous research undertakings in this area to increase the acid resistance of concrete by use of different cements, pozzolans and polymer and geopolymer concretes, still for highly acidic environments (pH < 4), construction has to be avoided often or high cost of repair and maintenance is imposed. Hence, this paper as one in the series of research undertaken on development of novel concretes for special applications, investigated the microstructure of an acid resistant concrete subjected to accelerated laboratory testing environment (7% sulphuric acid) and its effect on the ductility of concretes in MOR tests.

Different methods were used to investigate the microstructures of the new acid resistant concrete (ARC) and conventional concrete (CC). The main findings of this study are as follows;

- Generally, after acid exposure, the surface of CC samples was degraded and washed away, whereas, despite the penetration of sulphur in external layers of ARC, it did not lose any paste from the exposed surface and it was not decomposed.
- After exposure to acid more microcracks developed in the paste of CC and ARC. This fact and crack bridging role of fibres seem to increase the ductility of samples in MOR test.
- Ettringite was not found in CC and ARC samples after exposure to acid. It might have been there at initial stages of exposure to acid and higher pH values where it is stable in.
- Gypsum was observed in CC, mostly in ITZ around the aggregates, and its expansion increased microcracks and hence, caused loosening of aggregates that in most cases resulted in aggregate pulling out from the paste. This led to more corrosive agents to enter the intact layers of the sample which could accelerate the deterioration.
- Despite the destructive effect of gypsum in CC, it is believed that its degradation is due to the acid effect on the concrete, not the formation of gypsum due to penetration of sulphur.
- In acid affected layers of ARC also gypsum was found by SEM-EDS and x-ray mapping. The existence of gypsum was confirmed in acid affected layers of both CC and ARC in acid exposed layers by use of XRD. However, given the existence of very low amount of calcium hydroxide in ARC, less gypsum was formed in ARC compared to CC.
- Studying the development of a protective layer in the interface of ARC due to low Ca/Si ratio and more chemical products after exposure to sulphuric acid in ARC is in progress.

4 ACKNOWLEDGMENT

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