Degradation of self-compacting concrete (SCC) due to sulfuric acid attack: Experiment investigation on the effect of high volume fly ash content

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Abstract. Concrete is susceptible to a variety of chemical attacks. In the sulfuric acid environment, concrete is subjected to a combination of sulfuric and acid attack. This research is aimed to investigate the degradation of self-compacting concrete (SCC) due to sulfuric acid attack based on measurement of compressive strength loss and diameter change. Since the proportion of SCC contains higher cement than that of normal concrete, the vulnerability of this concrete to sulfuric acid attack could be reduced by partial replacement of cement with fly ash at high volume level. The effect of high volume fly ash at 50-70% cement replacement levels on the extent of degradation owing to sulfuric acid will be assessed in this study. It can be shown that an increase in the utilization of fly ash to partially replace cement tends to reduce the degradation as confirmed by less compressive strength loss and diameter change. The effect of fly ash to reduce the degradation of SCC is more pronounced at a later age.

1. Introduction
Concrete is a construction material that has been applied in the development of many types of infrastructures. These infrastructures have been designed, built and maintained to meet certain service life. However, many of these infrastructures have no longer in use before reaching their respective service life. The root of the problem could be due to the degradation of concrete material which eventually affects serviceability and capacity of structural concrete. Therefore, identifying the cause and rate of concrete degradation will aid the engineers to design, build and maintain a better structural concrete for a sustainable infrastructure.

Deterioration or degradation of concrete is any adverse change in normal, mechanical, physical dan chemical properties either on the surface or in the body of concrete, generally due to the disintegration of its components. The effect of deterioration may or may not be manifested visually. The following are three basic visual symptoms of distress in structural concrete: cracking, spalling and disintegration [1]. Aggressive agents from the environment could initiate a chemical attack on the concrete leading to the distress. The present of sulfuric acid produced from either sewage or sulfur dioxide in the atmosphere of industrial cities are examples of an aggressive agent that could be the source of the chemical attack on concrete. The attack is due to the high alkalinity of portland cement, which can react with the sulfuric acid [2]. Calcium hydroxide of the hydrated portland cement first reacts with sulfuric acid to produce gypsum in which the formation of gypsum is accompanied by volume
expansion. The expansion initiates distress in the brittle hardened concrete leading to cracking. The second reaction is a reaction between gypsum and calcium aluminate of hydrated portland cement. This second chemical reaction forms ettringite which instigates even greater expansion. At a high alkalinity or lower pH (less than 11.5-12) ettringite is destabilized and decomposed into softer gypsum. At this high alkalinity, concrete is also susceptible to acid attack in which calcium silicate hydrate is decalcified leading to the disintegration of concrete [3]. The deterioration process leads to physical, mechanical and chemical changes on concrete on which sulfuric acid attack may be quantified in the laboratory. Most common practices to measure a sulfuric acid attack on concrete are by quantifying mass loss, dimension change, strength loss, and sulfur concentration in the attacked concrete [2].

The resistance of concrete to sulfuric acid attack is subject to concrete composition especially that of cement type. This is due to the fact that reactions with respect to sulfuric acid attack involve hydrated portland cement. An attempt had been made to reduce the C₃A content of portland cement to obtain sulphate-resistant portland cement (SRPC). ASTM C 150 Type II and ASTM C 150 Type V is an example of such cement for moderate and severe exposure to sulphate environment, respectively. These cement may be used to substitute ordinary portland cement (OPC) in order to reduce the degradation of concrete in the sulfuric acid environment. However, as shown by Attiogbe and Rizkalla [2] prolonged exposure periods does not appear to provide a better resistance to sulfuric acid attack. This is because sulphate attack is only one aspect of sulfuric acid on concrete. The reaction of the acid with calcium silicate hydrate is another aspect of sulfuric acid attack that should be of concern. Another attempts to increase concrete resistance against sulfuric acid attack are by incorporating mineral admixtures such as fly ash, ground granulated blast furnace slag (GBS), silica fume and metakaolin into the concrete composition. The inclusion of mineral admixtures could be that of used as partial cement replacement, mineral addition, binary blended cement or ternary blended cement[4-6]. The effect of mineral admixtures on the deterioration process of concrete due to sulfuric acid attack provide an opportunity for researchers to create or modify concrete composition which can be durable in the sulfuric acid environment.

In the construction industry, a special type of concrete i.e. self-compacting concrete (SCC) has been introduced to overcome the problem of placing and compacting fresh concrete in highly-reinforced members and another area that can not be accomplished using a conventional concreting method. Fresh properties of SCC should meet the following criteria: flowability, filling ability and passing ability under its own weight without a tendency to segregation. With these fresh properties, once it is discharged from the mixer into formwork, it will flow and fill all recesses, reinforcement spaces and voids under its own weight and be self-compacted without any external aid of vibration. The key parameter to obtain SCC is moderate viscosity which can be achieved by a higher composition of fine components, the use of superplasticizer and sometime viscosity agent. SCC tends to have a higher cement content than conventional concrete. For this reason, mineral admixtures may be used as partial cement replacement. This research uses fly ash as partial cement replacement in producing SCC. The replacement level is in the range of 50-70%. Hence, the concrete investigated in this research fall into the category of high volume fly ash-self compacting concrete (HVFA-SCC).

Partial substitution of cement with mineral admixtures in SCC is beneficial with regard to improving the durability of this concrete. It has been noted by other investigators [4] that lowering cement content by incorporating fly ash as partial replacement tends to increase its resistant to sulfuric acid as measured by the mass loss. The increase in the resistance could be due to two factors i.e. a decrease in the actual cement content in the concrete composition and an increase in the formation of C-S-H as a result of the pozzolanic reaction. The first factor is evident from the fact that there is a lower mass loss of SCC with a lower strength (or with a lesser cement content) compared to that of SCC with a higher strength (or with a greater cement content). The sulfuric acid attack is primarily related to chemical reactions between a sulfuric acid and hydrated cement. Hence, a higher cement content in the concrete composition means more hydrated cement (calcium hydroxide and calcium aluminate) are available for sulphate reactions converting the solid products of cement hydration into...
softer gypsum. For SCC mixture with a pozzolanic addition such ash fly ash, the increased formation of C-S-H promotes refinement of porosity and additional binding property. These could be responsible to the more resistant of SCC containing fly ash to the acidic reaction when this concrete exposed to sulfuric acid. Other investigators [3] show different results in term of the effect of fly ash on the resistance of SCC to sulfuric acid attack. The refinement of capillary pores and eventually a reduction in the total porosity of SCC containing fly ash has negative consequences to sulfuric acid attack. This is due to pores densification creates fewer spaces to accommodate stresses induced by expansion of gypsum as a product of sulphate reaction. Hence, there is a competition between the deterioration process in SCC containing fly ash owing to sulphate attack and acid attack with regard to the effect of refinement porosity.

It should be noted that pozzolanic reaction in concrete containing fly ash takes place at a later age (more than 90 days). Thus, refinement of porosity is not gained at an early age. This is in line with the results of Sunamasto and Kristiawan [7] who confirm that inclusion of high volume fly ash at an early age tends to increase porosity. At an early age, this type of concrete turns out to be more resistant to sulfuric acid attack compared to that of SCC with a lower amount of fly ash [8]. The effect of high volume fly ash in SCC with respect to sulfuric acid attack is further investigated in this research. The varying parameter subjected to this investigation is fly ash content. The effect of sulfuric acid is observed in term of strength loss and dimension (diameter) change.

2. Materials and Method

2.1. Materials

Coarse aggregate (CA) with a maximum size of 10 mm was used in the production of SCC. The aggregate has been subjected to various tests following ASTM C127, ASTM C131 and ASTM C136 to determine its specific gravity, resistance to degradation and gradation, respectively. It was confirmed that this aggregate conforms to the requirements for grading and quality of aggregate as specified by ASTM C33. The fine aggregate or sand (S) was also subjected to various tests which include specific gravity, gradation, organic impurities and clay particles content according to ASTM C127, ASTM C136, ASTM C40 and ASTM C117, respectively. The S conforms to all requirements for grading and quality of aggregate as specified by ASTM C33. Cement used in this research was ordinary portland cement (OPC) or type I cement. Fly ash (FA) was obtained from a power plant in Cilacap. This fly ash is that of Class C as specified by ASTM C618.

All the ingredients for producing SCC was proportioned following the recommendation by Ozawa and Okamura [8]. The key factors to obtain SCC as stated in the recommendation are: the volume of CA is limited to 50% of the total solid volume; S used is no more than 40% of the total mortar volume; volume ratio of water/binder (W/B) is in the range of 0.9-1; and finally, the superplasticizer (Sp) dosage is determined to meet the self-compacting concrete. Based on these guidelines, after few trials the following initial proportion was obtained as per m³ of SCC: 738 kg of OPC, 579 and 703 kg of S and CA, respectively, 211 kg of W and finally 7.27 kg of Sp. The amount of OPC was then reduced by FA substitution at 50-70% by weight of OPC. The final mixtures proportion is given in Table 1.

| ID  | OPC (kg) | S (kg) | CA (kg) | W (kg) | Sp (kg) | FA (kg) |
|-----|----------|--------|---------|--------|---------|---------|
| C50%| 369      | 579    | 703     | 211    | 7.37    | 369     |
| C55%| 332      | 579    | 703     | 211    | 7.37    | 405     |
| C60%| 295      | 579    | 703     | 211    | 7.37    | 442     |
| C65%| 258      | 579    | 703     | 211    | 7.37    | 478     |
| C70%| 221      | 579    | 703     | 211    | 7.37    | 516     |
2.2. Methods
Cylinder specimens of 150x300 mm were cast. For each mix proportion, 12 cylinder specimens were prepared. On the following day, these cylinders were removed from their casting molds, and immediately a half of these cylinders were immersed in a tank containing 5% concentration of the sulfuric acid solution and the other half were immersed in water. To maintain the 5% concentration of sulfuric acid solution for the period of test, the solution was renewed every week. The immersion was carried out continuously until the cylinder specimens were tested in compression following ASTM C39 at the age of 28 and 90 days. The compressive strength of SCC was determined as average strength of three specimens. The strength loss of SCC due to sulfuric acid attack was determined using equation (1).

\[ C_l(\%) = \left( \frac{C_{wa} - C_{sa}}{C_{wa}} \right) \times 100 \]  

where \( C_l \) is strength loss (%), \( C_{wa} \) is the compressive strength of concrete immersed in water and \( C_{sa} \) is the corresponding compressive strength of concrete immersed in sulfuric acid.

The diameter of cylinder specimens that have been immersed in sulfuric acid solution were measured at 28 and 90 days to observed the physical degradation of SCC due to sulfuric acid attack. The physical degradation was quantified in term of changes in diameter of cylinder specimens which were determined using equation (2).

\[ D_e(\%) = \left( \frac{D_0 - D_{sa}}{D_0} \right) \times 100 \]

where \( D_e \) is a percentage of change in diameter after immersion in the sulfuric acid solution, \( D_0 \) is the original diameter of cylinder specimens before immersion i.e. 150 mm and \( D_{sa} \) is the diameter of cylinder specimens after immersion.

3. Results and discussion

3.1. Compressive strength
The compressive strengths of SCC containing various fly ash concentrated under immersion in 5% sulfuric acid solution for a period of 28 and 90 days are presented in figure 1. The corresponding compressive strengths of the SCCs immersed in water are given in the same figure for comparison and assessment of the strength loss. Comparison between compressive strength of SCC immersed in water and sulfuric acid solution reveals the effect of sulfuric acid attack to deteriorate concrete. It is clearly shown that reduction in compressive strength of SCC due to sulfuric acid attack is greater at a later age. The extent of reduction is also influenced by fly ash content. A higher fly ash content seems to be beneficial to increase the resistance of SCC to sulfuric acid attack as indicated by a lesser compressive strength loss (see figure 2). At an early age, however, the influence of fly ash content appears to be inconsistent. The different tendency of the effect of fly ash content on compressive strength loss due to sulfuric acid attack may be attributed to the pozzolanic reaction.

It is recognized that pozzolanic reaction takes places in the hardened state, and the beneficial effect of this reaction effectively observes at a later age (90 days). The conversion of CaOH into C-S-H as a result of pozzolanic reaction contributes to an increase in strength and reduction in porosity [9-10]. The effect of pozzolanic reaction to increase the compressive strength of SCC investigated in this study may be observed by comparing the strength of SCC immersed in water for 28 and 90 days. It is indicated that prolonging period of immersion in water increases compressive strength especially on SCC with higher fly ash content. On the other hand, prolonging immersion of SCC in sulfuric acid solution tends to decrease the compressive strength of lower fly ash content [2,11]. At higher fly ash content, the reduction in compressive strength due to sulfuric acid is surpassed by the pozzolanic reaction effect. Thus, the final compressive strength of SCC with higher fly ash contents turns to be
increased when the comparison is made between those immersed in sulfuric acid for 28 and 90 days. All of these lead to the following findings: at low fly ash content prolonging period of immersion in water and in sulfuric acid causes an increase and decrease of compressive strength, respectively. The different in compressive strength between SCC containing low fly ash immersed in water and sulfuric acid for a longer period becomes greater than that immersed for a shorter period. Thus, a greater compressive strength loss of SCC containing low fly ash content is significantly observed at longer immersion period. At high fly ash content prolonging period of immersion both in water and sulfuric acid tends to increase the compressive strength compared to the corresponding SCC immersed for a shorter period. Hence, at longer immersion period the observed strength loss of SCC at higher fly ash content is lesser than at lower fly ash content. The overall effect of fly ash content may be summarized as follows: at a longer period of immersions, compressive strength loss is reduced when higher fly ash content is incorporated in SCC.

![Figure 1](image-url)  
**Figure 1.** The compressive strength of SCC with various fly ash content determined after 28 (a) and 90 (b) days immersion in water and 5% sulfuric acid solution.

![Figure 2](image-url)  
**Figure 2.** Percentage of compressive strength loss due to sulfuric acid attack

3.2. Diameter change
The effect of the sulfuric acid attack on concrete can also be observed on the basis of changes in dimensions. The changes in dimensions indicate the extent of physical degradation owing to sulfuric acid attack. In this investigation, the physical degradation of SCC with various fly ash contents is quantified on the basis of diameter changes. The result is presented in figure 3. There is a distinct
magnitude of diameter changes between SCC immersed in the sulfuric acid solution for 28 days period than that immersed for 90 days period. At shorter period the changes in the diameter are in the range of 1-3% while at the longer period the changes are in the range of 7-11%. The changes in diameter of SCC specimens exposed to sulfuric acid suggest that disintegration of the solid component of SCC has occurred. The disintegration is started in the outer zone of SCC specimens where there is direct contact with the sulfuric acid solution (see figure 4). The disintegration is continuous and goes inwards long as the specimens kept immersed in the sulfuric acid solution. The result is a reduction in diameter of specimens with time. It has been shown by other investigators [4,11] that beyond the depth of attacked zone concrete tends to maintain its solid properties since no degradation occurs in this unattacked zone.

Figure 3. Diameter change of SCC with various fly ash contents due to sulfuric acid attack

Figure 4. Disintegration of specimen at outer zone due to direct contact with sulfuric acid after immersed for 28 and 90 days

An increase in fly ash content has slightly reduced the degradation of SCC as observed from the diameter change with the exception for SCC containing 55% fly ash. Higher cement content of SCC (or lower fly ash content) could be responsible for this behaviour. Since more hydrated cement is available in SCC with higher cement (or lower fly ash) content, there is a higher probability of this
concrete to be severely attacked by sulfuric acid. For SCC containing 55% fly ash, the highest strength of this concrete may be due to minimum interparticle spaces at this replacement level (consequently minimum porosity) [7] in addition to the contribution of relatively still higher cement content for hydration to proceed. Hence, when this concrete is attacked by sulfuric acid, the pores system can not accommodate the crystal gypsum leading to induced stresses which eventually deteriorate this concrete more severely [3]. The result is the highest decrease in the diameter of SCC with 55% fly ash content.

4. Conclusions
Based on the experimental results it is concluded that the degradation of SCC due to sulfuric acid attack as measured by compressive strength loss and diameter change can be reduced with a higher inclusion of fly ash to replace partially cement. The extent of the reduced degradation is more pronounced at a later age. The effect of fly ash content to modify SCC resistance against sulfuric acid could be explained by the combination of lower cement content, pozzolanic reaction and refinement of interparticle spaces. Less cement content gives fewer hydrated cement that will be attacked by sulfuric acid. The pozzolanic reaction will improve the strength of concrete which eventually decreases the tendency of concrete to disintegrate owing to sulfuric acid attack. Refinement of interparticle spaces may cause detrimental effect as they can not accommodate stresses induced by expansion of gypsum.

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