EXPERIMENTAL STUDY ON CONCRETE FOR SULPHURIC ACID RESISTANCE USING SILICA FUME, GROUND GRANULATED BLAST FURNACE SLAG AND VOLCANIC ASH

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Abstract: Sulphuric acid corrosion is challenging problem particularly in sewer environments. In many of the industries sulphuric acid is used during procedure, which can lead to decrease of strength of the concrete structures. Then, it is very important to construct durable concrete structures in such procedures. An experimental study was under taken to improve concrete resistance against sulphuric acid attack. Five concrete mixtures were used in the present study, first mix consists ordinary Portland cement (OPC) as a control mix and the second one consists 10% replacement of cement with silica fume. Third mix consists ordinary Portland cement with 10% ground granulated blast furnace slag (GGBS) and forth mix consists OPC with 15% replacement of GGBS. Other mixes contain OPC with 10% and 15% replacement of volcanic ash. The thick packing of siliceous aggregates and cement materials were used to achieve the high density of concrete. In the present study, concrete cubes were immersed in 15% sulphuric acid of pH=1.0. They were tested for compression test up to 90 days. The compressive strength of other mixtures was better than the control mixture.

Keywords: GGBS, Silica fume, Sulphuric acid, volcanic ash

I. INTRODUCTION
Concrete is the mainly used construction material for sewer structures. However, the environment in some sewer structures can become very acidic due to mainly formation of sulphuric acid converted from hydrogen sulphide by bacterial action. Significant deterioration of concrete in such harsh environment has been reported all over the world. Also several reports were published elucidating the mechanisms of concrete deteriorations in sewer environments. Although, it has been reported that some new materials such as high performance coating, fibre glass reinforced lining, special mortars and high proportions of polymer modified binder can be more acid resistant, but they are costly for most practical applications. Therefore, the research on evaluation of acid resistance of normal concretes is still attractive.

The deterioration of wastewater infrastructure has long been a cause for concern but the issues surrounding the problem remained unknown for many years. Traditionally designed to resist high levels of sulphate attack, wastewater treatment systems are subjected to a considerably more aggressive form of deterioration – biogenic sulphuric acid corrosion. To this day the true mechanisms of attack have yet to be fully grasped by concrete specifies and this is evident in the poor state of infrastructure used in this environment. There is clearly a need to distinguish between the two forms of attack and the research conducted in this investigation shows that both the nature and severity of attack is drastically different. Existing methods aimed at counteracting the corrosive forces focus on remedial work, periodic maintenance and replacement of defective components. This is clearly not a cost effective practice especially considering that this form of attack can manifest itself within a relatively short period of time.

II. LITERATURE REVIEW
R. Sri Ravindrarajah says, “Sulphuric acid attack resulted in concrete disintegration at an almost constant rate, the hydrochloric acid attack rate was reduced with time, whereas the lactic acid attack resulted leaching of corrosion products, at a slower rate under stagnant condition”.

Anne-Micke (1967) studied “the deformations in more detail, the applicability of traditional creep and shrinkage models test series as described, the following conclusions can be formulated with increasing c/p ratio, and consequently increasing cement content and decreasing w/c ratio, a decrease of the creep deformations is found. The fineness of the tested fillers has almost no influence on the deformations”.

Audenaert K(1971) made “an extended experimental programme on chloride penetration of self compacting concrete mixtures and traditional concrete mixtures were determined. Based on these tests, the conclusion is that the penetration depth in real conditions is strongly influenced by water/cement and water/ (cement +filler) ratios. Decreasing one of these ratios or both is leading to as decreasing penetration depth”.

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O’Connell, M, McNally, C & Richardson, MG (2010) ‘Biochemical attack on concrete in wastewater applications: a state of the art review’ Cement and Concrete Composites. This paper was published in the peer-reviewed journal Cement and Concrete Composites and the full citation for the paper Torii and Kawamura, investigated the effect of using silica fume and fly ash as partial replacement for cement on the resistance of concrete to a 2% solution of sulphuric acid. They concluded that such a partial replacement for cement could not effectively prevent the acid-type deterioration involving surface scaling and softening of mortar.

Jirasit suggested that concrete made with a cementitious material content of 300 kg/m3 and incorporating 50% fly ash as partial replacement for cement could resist a 3% H2SO4 solution.

Daczko argued that partial replacement of OPC by 8% silica fume could reduce the mass loss of concrete specimens immersed in an H2SO4 solution with a pH of 1 by 30%. They also argued that using 8% metakaolin as partial replacement for OPC provided little contribution to the resistance of concrete to sulphuric acid attack.

Attiogbe and Rizkallah reported that for prolonged exposure periods, sulphate-resistant Portland cement (SRPC) does not appear to provide a better resistance to sulphuric acid attack than that provided by ordinary Portland cement (OPC). This is because sulphate attack is only one aspect of sulphuric acid attack on concrete.

Parker identified Thiobacillus genus bacteria as the source of sulphuric acid formation at the crown of concrete sewer pipes. The most aggressive species of these bacteria is Thiobacillus thiooxidans, which was shown to grow well in the laboratory even when exposed to a 7% solution of sulphuric acid.

III. METHODOLOGY
The current work is aimed to study the properties of concrete by partially replacing cement by silica fume, ground granulated blast furnace slag and volcanic ash and compare the results between conventional and other material replaced concrete. In order to select the material for mix design, preliminary tests are conducted on materials such as cement, fine aggregate, coarse aggregate, silica fume, ground granulated blast furnace slag and volcanic ash. Different materials used in the work and their test results are presented below.

3.1 Materials Used
1. Cement (53 Grade OPC)
2. Fine aggregate (F.A)
3. Coarse aggregate (C.A)
4. Silica fume (S.F)
5. Ground granulated blast furnace slag (GGBS)
6. Volcanic Ash (V.A)
7. Water

3.1.1 Cement:
Ultra-tech OPC 53 grade was used. Cement procured from single source, properties of which are tested in the laboratory. Some of the Properties of cement are given below [IS: 12269-1987]

- Specific gravity 3.1
- Normal consistency 34%
- Fineness 2% (Should not exceed 10%)
- Initial setting time 40 minutes (Should not be less than 30 minutes)
- Final setting time 190 minutes (Should not exceed 600 minutes)

3.1.2 Fine Aggregate (F.A):
It is the aggregate most of which passes 4.75 mm IS sieve and contains only so much coarser as is permitted by specification. According to source fine aggregate may be described as

FIGURE 3.1: CEMENT FIGURE 3.2: FINE AGGREGATE
In the present study good quality zone-II fine aggregates were used of Specific gravity=2.61 and Bulk density=1710 Kg/m$^3$.

3.1.3 Coarse Aggregate (C.A):
It is the aggregate most of which is retained on 4.75 mm IS sieve and contains only so much finer material as is permitted by specification.

<table>
<thead>
<tr>
<th>Sieve Size, Mm</th>
<th>% Passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>100</td>
</tr>
<tr>
<td>12.5</td>
<td>35.7</td>
</tr>
<tr>
<td>10</td>
<td>7.0</td>
</tr>
<tr>
<td>6.3</td>
<td>1.0</td>
</tr>
<tr>
<td>4.75</td>
<td>0</td>
</tr>
</tbody>
</table>

In the present investigation aggregate available from local crusher was used. Two size fraction i.e. 20mm and 10mm size coarse aggregate was used and its specific gravity=2.8, bulk density=1480 Kg/m$^3$.

3.1.4 Silica Fume (S.F)
Silica fume not only provides an extremely rapid pozzolanic reaction, but it’s very fine size also provides a beneficial contribution to concrete. Silica fume tends to improve both mechanical properties and durability. Silica fume concretes continue to gain strength under a variety of curing conditions, including unfavourable ones. Thus the concretes with silica fume appear to be more robust to early drying than similar concretes that do not contain silica fume.

3.1.5 Ground Granulated Blast Furnace Slag (GGBFS):
Ground-granulated blast-furnace slag (GGBS or GGBFS) is obtained by quenching molten iron slag (a by-product of iron and steel-making) from a blast furnace in water or steam, to produce a glassy, granular product that is then dried and ground into a fine powder. The chemical composition of a slag varies considerably depending on the composition of the raw materials in the iron production process. Silicate and aluminates impurities from the ore and coke are combined in the blast furnace with a flux which lowers the viscosity of the slag.

Typical chemical composition:
- Calcium oxide = 40%
- Silica = 35%
- Alumina = 13%
- Magnesia = 8%

Typical physical properties:
- Colour: off white
- Specific gravity: 2.9
- Bulk density: 1200 Kg/m$^3$
- Fineness: 350 m$^2$/kg
3.1.6 Volcanic Ash (V.A)
Volcanic ash consists of particles with diameters <2 mm (particles >2 mm are classified as lapilli) and can be as fine as 1 μm. The density of individual particles varies with different eruptions. The density of volcanic ash varies between 700–1200 kg/m³. The main chemical elements contained in volcanic ash, are siliceous and oxygen, which constitute the main components of minerals and rocks in the Earth’s crust and mantle.

Table 3.4: Chemical Composition Of Volcanic Ash

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>65</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>18</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5</td>
</tr>
<tr>
<td>MgO</td>
<td>2</td>
</tr>
<tr>
<td>CaO</td>
<td>4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4</td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
</tr>
</tbody>
</table>

3.2 SULPHURIC ACID ATTACK
Sulphuric acid attack is very damaging to mortar as it combines an acid attack and a sulphate attack. At the first stage, deterioration of Ca(OH)₂ results in an expansive gypsum formation. The gypsum then reacts with C₃A in aqueous environment and forms a more expansive product called ettringite. These very expansive compounds cause internal pressure in the mortar, which leads to the formation of cracks and the transformation of the mortar into a mushy or a non-cohesive mass.

Sulphuric acid may also cause the decalcification of Calcium silicate hydrates C-S-H and will ultimately transform the C-S-H into amorphous hydrous silica. The following equations express these reactions:

\[
\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} \quad \text{(Gypsum)}
\]

\[
3(\text{CaSO}_4.2\text{H}_2\text{O}) + 3\text{CaO}.\text{Al}_2\text{O}_3.12\text{H}_2\text{O} + 14\text{H}_2\text{O} \rightarrow 3\text{CaO}.\text{Al}_2\text{O}_3.3\text{CaSO}_4.32\text{H}_2\text{O} \quad \text{(Ettringite)}
\]

\[
\text{CaO.} \text{SiO}_2.2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{Si (OH)}_4 + \text{H}_2\text{O} \quad \text{(Hydrous silica)}
\]

IV. DIFFERENT MIXES:

Table 3.5: Different Mix Used For Project

<table>
<thead>
<tr>
<th>Mix</th>
<th>TYPE OF MIX</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Control Mix</td>
</tr>
<tr>
<td>II</td>
<td>10% Replacement Of Cement With Silica Fume</td>
</tr>
<tr>
<td>III</td>
<td>10% Replacement Of Cement With GGBS</td>
</tr>
<tr>
<td>IV</td>
<td>15% Replacement Of Cement With GGBS</td>
</tr>
<tr>
<td>V</td>
<td>10% Replacement Of Cement With Volcanic Ash</td>
</tr>
<tr>
<td>VI</td>
<td>15% Replacement Of Cement With Volcanic Ash</td>
</tr>
</tbody>
</table>

4.1 TESTS ON FRESH CONCRETE:
Slump cone test and compressive strength test was conducted on M40 grade of concrete in fresh state.

4.1.1 Slump Cone Test:
The test is popular due to the simplicity of apparatus used and simple procedure. Unfortunately, the simplicity of the test often allows a wide variability in the manner that the test is performed. It was observed from the slump cone test which is a test conducted to measure the workability of the concrete, the workability of concrete with the replacement of silica fume, ground
granulated blast furnace slag and volcanic ash was better than the normal concrete mix. Different sizes of slump observed for different mixes are given below:

<table>
<thead>
<tr>
<th>MIX</th>
<th>SLUMP SIZE(cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6</td>
</tr>
<tr>
<td>II</td>
<td>4</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
</tr>
<tr>
<td>IV</td>
<td>3</td>
</tr>
<tr>
<td>V</td>
<td>5</td>
</tr>
<tr>
<td>VI</td>
<td>4</td>
</tr>
</tbody>
</table>

### 4.1.2 Preparation of Specimens

Moulds of standard size 150 mm X 150 mm X 150 mm were used for casting the cubes. The internal surfaces of moulds are cleaned and one coat of cutting oil is applied. The moulds are filled in three layers and the height of each layer is about 1/3rd height of mould, each layer is compacted by giving 25 blows with a tamping rod over the entire cross section of the mould uniformly. After filling and compacting the moulds, the top surface are made smooth and kept for a period of 24 hours. Then the mould is removed and the cubes are kept under water for 7, 14, 28, 56, and 90 days. The curing of specimens is done by pounding method of curing. Water should be clean and free from impurities and 15% of pH 1 sulphuric acid is added to the water. Then after completing the curing period all the specimen were removed and kept for drying for one day. The surface of the specimens should be cleaned and the test is carried out. 30 numbers of cubes were being cast for compressive strength test for M40 grade concrete. The total number of specimens casted for M40 grade concrete is shown in table.

<table>
<thead>
<tr>
<th>Mix</th>
<th>% Of Replacement</th>
<th>No Of Specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td>10% SF</td>
<td>5</td>
</tr>
<tr>
<td>III</td>
<td>10% GGBS</td>
<td>5</td>
</tr>
<tr>
<td>IV</td>
<td>15% GGBS</td>
<td>5</td>
</tr>
<tr>
<td>V</td>
<td>10% VA</td>
<td>5</td>
</tr>
<tr>
<td>VI</td>
<td>15% VA</td>
<td>5</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

### V. RESULTS AND DISCUSSIONS

From the test results of compressive strength for M40 grade concrete, it is found that the compressive strength has increased with the replacement of silica fume, ground granulated blast furnace slag and volcanic ash content up to 15% then the strength decreased because of the degradation of concrete by sulphuric acid. It is found that the optimum percentage dosage of 15% of volcanic ash which gives the max compressive strength for M40 grade concrete.

The resistance to sulphuric acid solution was measured by means of the weight loss of the mortar cubes. The weight loss is considered as a function of time. As expected, the sulphuric acid resistance of mortars improved with increasing the replacement level of volcanic ash. This improvement of acid resistance was higher at early ages and decreased with increasing the immersion time. Beyond 28 days of exposure, slight improvements in the sulphuric acid resistance have been found.
Furthermore, the pozzolanic reaction fixes Ca(OH)\textsubscript{2}, which is usually the most vulnerable product of hydration of cement insofar as acid attack is concerned. Contrary to expectation, the weight loss of cement replaced mortars was very similar to that of control mix mortars under similar conditions. This is possibly because the hydrated silica fume, ground granulated blast furnace slag, volcanic ash and cement mortars both contain Portland and calcium silicates in large proportions.

It should be also noted that after 90 days of exposure to sulphuric acid, cement replaced mixes and, to a smaller degree, cement without replacement mortar cubes showed a surface layer of brown colour. This brown-coloured layer, which is probably composed of ferric oxides, can be attributed to the higher content of C\textsubscript{4}AF in both cements. Further, sulphuric acid attack on mortars was associated with erosion and softening due to leaching of Ca and decalcification of C-S-H.

Table 5.1: Compression Strength Of Concrete

<table>
<thead>
<tr>
<th>MIX</th>
<th>COMPRESSION STRENGTH OF CONCRETE (MPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 DAYS</td>
</tr>
<tr>
<td>I</td>
<td>25.0</td>
</tr>
<tr>
<td>II</td>
<td>30.5</td>
</tr>
<tr>
<td>III</td>
<td>31.3</td>
</tr>
<tr>
<td>IV</td>
<td>30.4</td>
</tr>
<tr>
<td>V</td>
<td>31.6</td>
</tr>
<tr>
<td>VI</td>
<td>32.5</td>
</tr>
</tbody>
</table>

Graph 5.1: Comparison Of Compressive Strength

**CONCLUSION**

1. For replacing cement by silica fume, ground granulated blast furnace slag, volcanic ash the optimum value is given by 15% replacement of volcanic ash.

2. The workability of concrete increased with the 10% replacement of cement by silica fume, and 10% and 15% replacement by ground granulated blast furnace slag, and volcanic ash.

3. It is found that there was 9% to 16% increment in compressive strength for M40 grade concrete when cement is replaced with silica fume, ground granulated blast furnace slag and volcanic ash at 7 days of curing.

4. It is found that there was 10% to 20% increment in compressive strength of concrete when cement is replaced with silica fume, ground granulated blast furnace slag and volcanic ash at 28 days of curing.

5. It is found that there was 11% to 20% increment in compressive strength of concrete when cement is replaced with silica fume, ground granulated blast furnace slag and volcanic ash at 90 days of curing.

6. It is found that degradation of concrete due to curing in sulphuric acid was high for control mix where as when cement is replacement with 10% of silica fume, 10% and 15% of ground granulated blast furnace slag and volcanic ash was more durable.

7. Durability of concrete was high for 15% replacement of volcanic ash.

8. Strength of compression was maximum for 15% replacement of cement with volcanic ash.

**FUTURE SCOPE**

Following are the scope for future work.
1. In the present work M40 grade of concrete is studied further work can be carried out on the higher grades of concrete and also M20, M25, M30, M35 grade.

2. Ground granulated blast furnace slag can be used as a partial replacement for fine aggregates.

3. Flexure behaviour of larger size beams can be studied.

4. Durability studies like Water absorption, Porosity, Resistance to abrasion etc can be carried out.

5. Admixtures like Silica fume, ground granulated blast furnace slag, and volcanic ash can also be further replaced partially by 20%, 25%, 30%, 35%, 40% etc.

REFERENCES


