Experimental study on durability assessment of concrete structures due to various chemical attacks

Venkatesh B. Panmand
venkatesh_panmand02@yahoo.com
Dr. D. Y.Patil School of Engineering, Pune, Maharashtra

Dr. Sanjay Kulkarni
sanjay_kulkarni.sk@gmail.com
Dr. D. Y.Patil School of Engineering, Pune, Maharashtra

ABSTRACT

The strength and durability of concrete after casting changes at variance factors regarding physical and chemical damages. Concrete structures with steel-reinforcement are in a continuous and losing life with corrosiveness that naturally occurs from long-term exposure to an aggressive environment. The concrete structure like dams, canals, bridges which have the influence of water forms various types of chemical reactions which include carbonation attack, sulfate attack, chloride attack, alkali-aggregate reaction, etc. Chemical reactions, either intrinsic or extrinsic, are one of the main reason for concrete’s deterioration. The present dissertation consists of an analysis of the chemical expansive reactions in concrete element, the alkalis aggregate reaction, and the internal sulfuric reaction. During the carbonation process, the fundamental element identified in the concrete microstructure is calcite which comes out at the surface of concrete structure, in the form of cracks. When carbon dioxide causes by environment come contact into the concrete structure and effect with calcium hydroxide to create calcium carbonate this phenomenon is called as carbonation. Carbonation usually describes by ph value which indicates the depth of reaction in the structure. The depth of carbonation directly affects the life of the structure in the year. Through the years to overcome this problem the solution is being discovered by performing various experiments on Concrete after and before the casting. Which gave us the Chemical test like by increasing the CO₂ binding capacity, improving CaO Value and physical tests such as applying an epoxy coating, etc. After all, performing the various types of test for a particular outcome finally check for durability tests for the concrete structure is taking place for better result. There are many of them but in this case, it will be ph indicator, UTM and CTM are being discussed. This project address the study of chemical reaction which is taking place on various type of concrete structures and affect the durability and strength of it.

Keywords — Sulphur, Chloride, Deterioration, Durability, Strength

1. INTRODUCTION

Concrete has long been used in the civil engineering industry for the construction of foundations, footings, retaining walls, slabs, pavements, tunnels, bridges, basins, canals, dams, drains, sewerage lines and many other structures and structural members. Concrete is the backbone of any country’s infrastructure. Concrete hardens and gains strength within days. Its relatively low cost, ease of application and relatively long term service life compared to other materials is the main cause of its popularity. The disadvantage of using concrete is that the microstructure of concrete allows the penetration of water and other destructive species that will cause premature failing of the concrete surface. A permeable concrete will allow infiltration of aggressive agents (chlorides, carbon dioxide and acids) to the steel reinforcement bars causing complete failure of the structure.

In general, concrete has a low resistance to chemical attack. The common forms of a chemical attack on concrete and the embedded reinforcement in reinforced concrete are chloride attack, sulphate attack, Carbonation due to Carbon dioxide, Alkali-aggregate reactions and acid attack. Concrete is susceptible to attack by sulfuric acid produced from either sewage or sulfur dioxide present in the atmosphere of industrial cities. This attack is due to the high alkalinity of Portland cement concrete, which can be attacked by other acids as well. Sulfuric acid is particularly corrosive due to the sulfate ion participating in sulfate attack, in addition to the dissolution caused by the hydrogen ion. Since sulfur compounds are formed as a result of the sulfuric acid–cement paste reaction, the increase in the sulfur content of concrete specimens could be used as a measure of the chemical manifestation of deterioration. In previous studies, weight loss, reduction in compressive strength, and change in dynamic modulus of elasticity were used to evaluate the extent of concrete deterioration due to sulfuric acid attack. These studies indicate that damage starts at the surface of the concrete and progresses inward. However, the extent of the damage along the depth of penetration of acid is not clearly defined. This information is necessary to accurately estimate the minimum thickness of the concrete cover in reinforced concrete structures or to adequately design for sacrificial layers in concrete structures exposed to sulfuric acid solutions.
As expected, the previous studies have generally shown that weight loss of the test specimens increases with a decreasing pH level of the acid solutions. However, in a recent study,’ a solution with a pH of 3 produced a greater weight loss than one with a pH of 2. This apparent anomaly needs to be resolved for an adequate comparison of the resistance of different concrete mixes to acid attack. The present study is aimed at evaluating the response of different concrete mixes to sulfuric acid attack, using both physical and chemical indicators of the degree of deterioration. An accelerated laboratory test program was conducted. The program involved alternate acid immersion and drying of test specimens, as well as continuous acid immersion of other test specimens. Changes in weight and thickness of the test specimens were used to evaluate the physical degree of deterioration of the concrete, while the increase in sulfur content of the test specimens, as measured with a Scanning Electron Microscope (SEM) equipped with an energy dispersive x-ray analyzer, was used to evaluate the chemical change in the concrete. Photomicrographs of the test specimens were used to study the extent of the acid attack.

Chlorides in de-icing salts or in soils, sea water and ground water can enter concrete and destroy the passive oxide film, which normally protects the steel against corrosion. Chloride can enter either through its ingredients (like chloride containing aggregates, and water) or through the environment (such as de-icing salts or seawater). As a result, rust layers build up on steel, whose volume is enough to exert disruptive tensile stresses on surrounding concrete causing it to crack or even spall.

Sulphates present in soils, groundwater and seawater react with Tricalcium Aluminate (C3A) of cement to form expansive compounds. The reaction leads to an increased volume of the products resulting in disintegration of the concrete. Sulphate resisting cement, which has a lower content of C3A (Type V cement) is best suited in conditions where an extensive exposure to sulphates is expected.

The pore solution of concrete is alkaline in nature due to the presence of portlandite or Calcium hydroxide (Ca(OH)₂). This alkaline solution protects steel from corrosion. The presence of CO₂ may lead to the destruction of this alkalinity. This process of loss of alkalinity due to the reaction between Ca(OH)₂ in concrete and CO₂ from air is known as carbonation. Carbonation leads to the formation of Calcium Carbonate and water, as a result, the alkalinity of concrete is lost. The steel thus becomes vulnerable to rusting in the presence of oxygen and moisture.

The reaction between the silica of aggregates (in siliceous aggregates) and the alkali content in cement is called alkali-aggregate reaction. The product of the reaction expands by absorbing water and increases in volume leading to cracking of concrete. Concrete is alkaline in nature due to the presence of Calcium Hydroxide (Ca(OH)₂). If attacked by an acid HX (where X is the negative ion of the acid), the components of the cement matrix break down in accordance with the following famous acid-base reaction:

$$2 \text{HX} + \text{Ca(OH)}_2 \rightarrow \text{CaX}_2 + 2 \text{H}_2\text{O}$$

The decomposition of the concrete depends on the porosity of the cement paste, on the concentration of the acid, the solubility of the acid calcium salts (CaX₂) and on the fluid transport through the concrete. Insoluble calcium salts may precipitate in the voids and can slow down the attack. Acids such as nitric acid, hydrochloric acid and acetic acid are very aggressive as their calcium salts are readily soluble and removed from the attack front. Other acids such as phosphoric acid and humic acid are less harmful as their calcium salt, due to their low solubility, inhibits the attack by blocking the pathways within the concrete such as interconnected cracks, voids and porosity. Sulphuric acid is very damaging to concrete as it combines an acid attack and a sulfate attack.

2. ATTACKS ON CONCRETE
2.1 Sulphur attack

Sulphate attack on concrete is a chemical breakdown mechanism where sulphate ions attack components of the cement paste. The compounds responsible for sulphate attack on concrete are water-soluble sulphate-containing salts, such as alkali-earth (calcium, magnesium) and alkali (sodium, potassium) sulphates that are capable of chemically reacting with components of concrete. Sulphate attack on concrete might show itself in different forms depending on:

- The chemical form of the sulphate
- The atmospheric environment which the concrete is exposed to.
2.1.1 When sulphates enter into concrete
- It combines with the C-S-H, or concrete paste, and begins destroying the paste that holds the concrete together. As sulphate dries, new compounds are formed, often called ettringite.
- These new crystals occupy empty space, and as they continue to form, they cause the paste to crack, further damaging the concrete.

2.1.2 Sources of Sulphates in Concrete:
- Portland cement might be over-sulphated.
- Presence of natural gypsum in the aggregate.
- Admixtures also can contain small amounts of sulphates.
- Soil may contain excessive amounts of gypsum or another sulphate.
- Ground water is transported to the concrete foundations, retaining walls, and other underground structures.
- Industrial waste waters.

2.1.3 Chemical Process of Sulphate Attack: The sulphate ion + hydrated calcium aluminates and/or the calcium hydroxide components of hardened cement paste + water = ettringite (calcium sulfoaluminate hydrate)

\[
C_3A.C_s.H_{18} + 2CH + 2S + 12H = C_3A.3C_s.H_{32}
\]

\[
C_3A.CH.H_{18} + 2CH + 3S + 11H = C_3A.3C_s.H_{32}
\]

The sulphate ion + hydrated calcium aluminates and/or the calcium hydroxide components of hardened cement paste + water = gypsum (calcium sulphate hydrate)

\[
Na_2SO_4 + Ca(OH)_2 + 2H_2O = CaSO_4.2H_2O + 2NaOH
\]

\[
MgSO_4 + Ca(OH)_2 + 2H_2O = CaSO_4.2H_2O + Mg(OH)_2
\]

2.2 Chloride attack: Chloride attack on concrete is one of the important aspects of the durability of concrete. It primarily affects the reinforcement of concrete and causes corrosion. Chlorides can be introduced into the concrete either during or after construction as follows:
- Before construction Chlorides can be admitted in admixtures containing calcium chloride, through using mixing water contaminated with salt water or improperly washed marine aggregates.
- After construction Chlorides in salt or sea water, in airborne sea spray and from de-icing salts can attack permeable concrete causing corrosion of reinforcement.

The chloride in the presence of water and oxygen reacts with an alkaline protected layer around the reinforcement and removes it. Chloride Attack on Concrete Structures is one of the most important phenomena we consider when we deal with the durability of concrete.

Among all sources of failure of concrete structures, the chloride attack accounts 40% contribution. The main effect of chloride attack is the corrosion of reinforcement that induces the strength of the structure drastically.

2.2.1 Causes of Chloride Attack on Concrete Structures: The attack of chloride on concrete structures can be happened either from inside of the concrete or through the ingress of chloride from outside to the inside of concrete structures. The chlorides exist in concrete during the casting process due to the following reasons:
- Use of seawater for the concrete mixing process
- Use of calcium chloride as an additive to increase the setting time
- Use of aggregates that contained chlorides which were not washed for mixing
- Aggregates with chloride content more than the limit stated in the specification

The chlorides enter the concrete from the exterior environment to the concrete interior due to the following reasons:
- Exposure of concrete to seawater
- Use of salt to melt the ice
- Presence of chlorides in the substances placed for storage

Comparing both the means of chlorides, the chances of exterior chloride action are high. Most of the offshore structures are subjected to extreme chloride attacks. This induces reinforcement corrosion of structures. In reality, the action of chloride in inducing corrosion of reinforcement is more serious than any other reasons. One may understand that Sulphates attack the concrete whereas the chloride attacks steel reinforcements.

A protective oxide film is present on the surface of the steel reinforcement due to the concrete alkalinity. This layer is called passivity. The process of carbonation will affect this protective passivity layer. This layer can also be affected by the presence of chlorides in water or in oxygen.

3. PREVENTION OF ATTACKS
3.1 Prevention of Sulphuric Attack on Concrete Structures: The acid attack on concrete can be minimized by providing due consideration to concrete porosity. Lesser the porosity, lesser will be the chances of acid attack on concrete. In another way, the concrete resistance to acids can also be provided by giving its surface an acid resistant coating.
3.2 Prevention of Chloride Attack on Concrete Structures
Several methods are available in order to prevent the effect of chlorides on concrete structures. Some of them are:
- Increasing the cover over the reinforcement bar. This is the simplest way to prevent chloride attack. Studies have shown that an increase in cover by one inch can increase the life period of the structure by double.
- The rate of deterioration of the reinforcement under extreme conditions of chlorides can be prevented by having rebar coated by epoxy, having cathodic protection or by use of stainless steel-clad rebar.
- Another important way is to decrease the chloride ion ingress into the concrete by decreasing the permeability of the concrete. This will decrease the durability and the time, cost of expensive repairs.

4. RESULTS AND ANALYSIS
4.1 Casting of specimens
Concrete Cube specimens (150 x 150 x 150mm size)
Beam Specimen (150 x 150 x 700mm)
Cylinder specimens (150mm dia)

4.2 Sulphur attack

| Table 1: Compressive strength results for sulphur attack (N/mm²) |
|------------------------|----------------|----------------|----------------|
| Days                  | Conventional M30 | 0.35% Sulphur | Epoxy Coating |
| 7 Days                | 24.2            | 22.6          | 23.9          |
| 14 Days               | 27.6            | 25.8          | 27.8          |
| 28 Days               | 31.5            | 26.4          | 28.7          |

Fig. 2: Compressive strength results for sulphur attack (N/mm²)

| Table 2: Flexural test results for sulphur attack (N/mm²) |
|------------------------|----------------|----------------|----------------|
| Days                  | Conventional M30 | 0.35% Sulphur | Epoxy Coating |
| 7 Days                | 4.76            | 3.09          | 3.95          |
| 14 Days               | 5.01            | 3.85          | 4.24          |
| 28 Days               | 5.49            | 4.18          | 4.95          |

Fig. 3: Flexural Test Results for Sulphur Attack (N/mm²)

| Table 3: Split tensile strength test results for sulphur attack (N/mm²) |
|------------------------|----------------|----------------|----------------|
| Days                  | Conventional M30 | 0.35% Sulphur | Epoxy Coating |
| 7 Days                | 2.78            | 1.95          | 2.07          |
| 14 Days               | 3.22            | 2.68          | 2.96          |
| 28 Days               | 3.99            | 3.02          | 3.17          |
4.3 Chloride attack

Table 4: Compressive strength test results for chloride attack (N/mm²)

<table>
<thead>
<tr>
<th>Days</th>
<th>Conventional M30</th>
<th>0.35% Chloride</th>
<th>Epoxy Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 Days</td>
<td>24.7</td>
<td>22.2</td>
<td>23.7</td>
</tr>
<tr>
<td>14 Days</td>
<td>27.8</td>
<td>23.7</td>
<td>25.6</td>
</tr>
<tr>
<td>28 Days</td>
<td>30.5</td>
<td>25.9</td>
<td>28.9</td>
</tr>
</tbody>
</table>

Table 5: Flexural test results for chloride attack (N/mm²)

<table>
<thead>
<tr>
<th>Days</th>
<th>Conventional M30</th>
<th>0.35% Chloride</th>
<th>Epoxy Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 Days</td>
<td>4.68</td>
<td>3.07</td>
<td>3.41</td>
</tr>
<tr>
<td>14 Days</td>
<td>5.08</td>
<td>4.19</td>
<td>4.95</td>
</tr>
<tr>
<td>28 Days</td>
<td>5.77</td>
<td>4.71</td>
<td>5.19</td>
</tr>
</tbody>
</table>

Table 6: Split tensile strength test results for chloride attack (N/mm²)

<table>
<thead>
<tr>
<th>Days</th>
<th>Conventional M30</th>
<th>0.35% Chloride</th>
<th>Epoxy Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 Days</td>
<td>2.68</td>
<td>1.78</td>
<td>2.27</td>
</tr>
<tr>
<td>14 Days</td>
<td>3.14</td>
<td>2.51</td>
<td>2.93</td>
</tr>
<tr>
<td>28 Days</td>
<td>3.97</td>
<td>2.94</td>
<td>3.28</td>
</tr>
</tbody>
</table>
5. CONCLUSIONS
From experimental work and testing of specimen following conclusions have been concluded:

- After 28 days the compressive strength was found to be decreased by 16% when it was affected by 0.35% of Sulphur and by using epoxy coating compressive strength of concrete was found to be increased by 9%.
- After 28 days the flexural strength was found to be decreased by 23% when it was affected by 0.35% of Sulphur and by using epoxy coating flexural strength of concrete was found to be increased by 19.1%.
- After 28 days the split tensile strength was found to be decreased by 24% when it was affected by 0.35% of Sulphur and by using epoxy coating split tensile strength of concrete was found to be increased by 15%.
- After 28 days the compressive strength was found to be decreased by 15% when it was affected by 0.35% of Chloride and by using epoxy coating compressive strength of concrete was found to be increased by 12%.
- After 28 days the flexural strength was found to be decreased by 18% when it was affected by 0.35% of Chloride and by using epoxy coating flexural strength of concrete was found to be increased by 10%.
- After 28 days the split tensile strength was found to be decreased by 25% when it was affected by 0.35% of Chloride and by using epoxy coating split tensile strength of concrete was found to be increased by 12%.

6. REFERENCES
[5] Dr Anwar Khitab, Dr Mohsin Usman Qureshi, Mr Muhammad Nadeem, “Concrete against acid attack: Preventive measures”