Effect of Different Pozzolanic Admixtures on Sulfuric Acid Resistance of Concrete

Masoud Moradian ¹
Milad Hallaji ²
Behnam Kiani ³
Mohammad Shekarchi ⁴
Mehdi Nemati Chari ⁵

ABSTRACT

Sulfuric acid environment is one of the most aggressive conditions which puts the durability of concrete in danger in many industrial structures. In this study, 10×10 concrete cube specimens containing silica fume, zeolite and metakaolin and also control specimens were made all with a w/c ratio of 0.45. After 28 days of water curing, specimens were placed in sulfuric acid solutions with pH=1 and pH=2. In order to keep the pH of solutions in a constant value, daily pH control was performed and required amount of acid added to solutions to reach the desired pH (the increase of pH value is result of reaction between concrete and acidic solution). During exposure period, weight changes of specimens as well as sulfate penetration depth were measured for comparing the performance of different mixtures. The results revealed that concrete specimens including pozzolanic admixtures performed considerably better than ordinary concrete without pozzolan.

Keywords

Blended cement, Durability, Pozzolan, Sulfuric acid, Weight change.

¹ Research assistant, Construction Materials Institute (CMI), School of Civil Engineering, University of Tehran, Tehran, Iran, Corresponding author. Tel.: +98-21-88969112; Fax: +98-21-88959740.
E-mail addresses: mmoradian@ut.ac.ir, URL: http://cmi.ut.ac.ir
² Research assistant, Construction Materials Institute (CMI), School of Civil Engineering, University of Tehran, Tehran, Iran, mhallaji@ut.ac.ir
³ Research assistant, Construction Materials Institute (CMI), School of Civil Engineering, University of Tehran, Tehran, Iran, behnam_kiani@ut.ac.ir
⁴ Associate Professor, Director of Construction Materials Institute (CMI), School of Civil Engineering, University of Tehran, Tehran, Iran, shekarch@ut.ac.ir
⁵ Research assistant, Construction Materials Institute (CMI), School of Civil Engineering, University of Tehran, Tehran, Iran, chari@ut.ac.ir
1 INTRODUCTION

Concrete is the most widely used material in construction of structures. When concrete is exposed to environment containing sulfuric acid, it experiences severe deterioration due to neutralization reactions. Sulfuric acid reacts with the free lime [Ca(OH)$_2$] in the concrete forming gypsum (CaSO$_4$·2H$_2$O). Another destructive action is the reaction between calcium aluminate and the gypsum crystals. These two products form the less soluble reaction product ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O) [Moradian et al. 2010, Clifton and Ponnorsheim 1994]. Both gypsum and ettringite cause expansion which results in cracking of concrete [Bonakdar and Mobasher 2010]. The corroded surface becomes soft and white. When the corrosion continues, the corroded concrete structure loses its mechanical strength [Monteny et al. 2001].

To extend the life of concrete in acidic environment, it is essential to find a way to control these processes. The rate of deterioration depends on the concentration of sulfuric acid, ambient temperature, cement type, water to cement ratio, porosity and presence of admixtures [Tumidajski 1995]. Generally, adding pozzolan results in a concrete with a denser structure, better able to withstand sulfate attack, but it also reduces or eliminates the free, leachable calcium hydroxide [Pavlík and Uncík 1997].

Among all mineral admixtures, silica fume (SF) has found to have the best performance in resistance of concrete in acidic environment [Dazko et al. 1997]. The effect of silica fume on concrete microstructure is well reported in the literature. Silica fume is an artificial pozzolan that increases the compressive strength of concrete as a result of making stronger transition zone as well as the increase in the rate of hydration at early ages [Ghods et al. 2007, Shekarchi et al. 2009]. Metakaolin is silica based and active pozzolan product that improves the mechanical properties of concrete in both short and long term [Nai-qian et al. 1990; Liguori et al. 2004; Perraki et al. 2003]. The prefix Meta refers to the calcination of kaolinite at certain temperature and the production of Metakaolin.

However, there is another admixture which has not got enough attention and its ability to improve performance of concrete in aggressive environments has almost left unknown. Natural zeolite (NZ) is a crystalline mineral that has siliceous and aluminum oxide in its chemical compound that like other mineral admixtures produces more C-S-H gel through pozzolanic activity [Ahmadi and Shekarchi 2010]. It is enunciated that 10% replacement of zeolite could lead to the production of high quality concrete with lower water absorption, chloride ion diffusivity coefficient and permeability. Although the usage of superplasticizer to reach the required workability is imperative [Ahmadi and Shekarchi 2010]. The porosity reduction can only obtained by limited amount of zeolite replacement which is claimed to be about 15% [Poon et al. 1999].

2 EXPERIMENT PROGRAM

2.1 Used Materials

Calcereous aggregate was chosen for the concrete mixes. Using calcereous aggregates instead of siliceous type provides additional alkalinity of concrete and increases durability of concrete in sulfuric acid environment [Barnard 1967; Thistlethwayte 1972]. The chemical analysis of aggregate is presented in table 1. Three types of pozzolan including silica fume, Metakaolin and zeolite were used in order to perform the tests. Table 2 includes the chemical analysis of cement as well as pozzolanic materials.

<p>| Table 1. Chemical analysis of aggregate. |</p>
<table>
<thead>
<tr>
<th>Oxide</th>
<th>Fine aggregate (%)</th>
<th>Coarse aggregate (%)</th>
</tr>
</thead>
</table>
Table 2. Chemical analysis of cement and pozzolanic materials.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cement (%)</th>
<th>Silica Fume (%)</th>
<th>Metakaolin (%)</th>
<th>Zeolite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>22.71</td>
<td>93.16</td>
<td>51.85</td>
<td>67.79</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.91</td>
<td>1.13</td>
<td>43.87</td>
<td>13.66</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.93</td>
<td>0.72</td>
<td>0.99</td>
<td>1.44</td>
</tr>
<tr>
<td>CaO</td>
<td>59.55</td>
<td>-</td>
<td>0.2</td>
<td>1.68</td>
</tr>
<tr>
<td>MgO</td>
<td>2.81</td>
<td>1.6</td>
<td>0.18</td>
<td>1.6</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.32</td>
<td>-</td>
<td>0.01</td>
<td>2.04</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.87</td>
<td>-</td>
<td>-</td>
<td>1.42</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.99</td>
<td>0.05</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>L.O.I</td>
<td>2.31</td>
<td>1.58</td>
<td>0.57</td>
<td>10.23</td>
</tr>
</tbody>
</table>

2.2 Mix Design

The mix design is presented in Table 3. The water to binder ratio was kept 0.45 in all the batches and cubic 10×10×10 cm specimens were made for placing in the acid solution. Moreover, polycarboxylate superplasticizer was employed to reach the slump of near 20 cm.

Table 3. Concrete mix design.

<table>
<thead>
<tr>
<th>Code</th>
<th>Cement (Kg/m³)</th>
<th>W/C</th>
<th>Silica fume (% replacement)</th>
<th>Zeolite (% replacement)</th>
<th>Metakaolin (% replacement)</th>
<th>Slump (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>400</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>MSF</td>
<td>370</td>
<td>0.45</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>MZE</td>
<td>360</td>
<td>0.45</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>MME</td>
<td>360</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>21</td>
</tr>
</tbody>
</table>

2.3 Performed Tests

Concrete specimens were put in sulfuric acid solution after 28 days of moist curing. The pH of solutions were kept 1 by adding additional sulfuric acid. Figure 1 shows the pH increase of solution during a period of 150 days. The weight change and also sulfate penetration in depth of concrete were measures in order to compare the performance of each specimen. For weighing of specimens, they were taken out of the tanks and let them be out for 4 hours for drying of their surfaces. Then weighting was performed using digital balance. For measuring the depth of sulfate penetration, concrete powder samples were taken from four different depths of specimens. The sulfate measurement was performed using gravimetric analysis.
In addition, some specimens were put in a solution of the pH=2 and the visual observation were assessed for this group.

![Figure 1. pH change of solution.](image)

### 3 RESULTS AND DISCUSSION

As expected, the concrete surface was corroded uniformly because of the calcareous base of aggregate. Existence of gypsum is the sign of sulfuric acid attack occurrence. However, considerable amount of efflorescence dissolve in solution and disappear from the specimen surface because of strong sulfuric acid. But, gypsum is visible on the surface of specimens which were placed in solution with pH=2. Figure 2 shows the specimens appearance after 120 days of exposure in sulfuric acid solution with pH=1.

![Figure 2. Specimens after 120 days exposure in sulfuric acid (pH=1).](image)

The specimens are visually resemble and no definite conclusion could be drawn. However, the specimen containing zeolite seems to have more efflorescence on its surface. Figure 3 shows the weight change of specimens after 200 day (each data is the average of results of 3 specimens). After 200 days of exposure in sulfuric acid with pH of 1 no weight loss was observable in none of specimens. The weight gain could be the result of completion of hydration reaction and also filling of pores by expansive products like gypsum and ettringite. It is possible that they experience weight loss after an undetermined period.
The specimens made with metakaolin showed more weight gain compared to other pozzolanic material. Control specimens weight changed less than three other codes as well. It could be concluded that using pozzolans improves the resistance of concrete exposed to acidic environments.

![Graph](image1)

**Figure 3.** Weight change of specimens in acid sulfuric (pH=1).

Sulfate profiles in depth of concrete are presented in Fig. 4. This test could be more expressive than weight change of concrete. The surface sulfate in specimen congaing zeolite is more than others. However the amount of sulfate of this specimen in depth of concrete is less than three other specimens. This test could support the idea of confident using of zeolite for making resistant concrete in sulfuric acid environment. The control specimen showed the worst performance and this implies the necessity of using pozzolanic for controlling the rate of deterioration in acidic environment.

![Graph](image2)

**Figure 4.** Sulfate profile in depth of concrete.

It is noted that formation of effloresce on the surface of concrete decrease the rate of deterioration and could be a protective layer against aggressive agents. Figure 5 shows the formation of this layer on the surface of concrete in sulfuric acid with pH of 2. In the case that aggregates are calcareous, this layer is thicker and more considerable. However, effloresce in stronger acid solution dissolves rapidly and has less important effect.
4 CONCLUSIONS

Investigation of concrete in sulfuric acid is important for simulation of concrete in environments like sewage pipes or industrial plants. In this paper, three different pozzolans were tested for comparing the performance of them in sulfuric acid environment. Based on the results of tests, the following conclusions could be drawn:

• Calcareous aggregate improves the properties of concrete exposed to acidic environment, because calcareous aggregates provide more alkalinity for concrete.
• Pozzolans improves mechanical and durability properties of concrete. Using pozzolans is one of the easiest ways to increase the resistance of concrete in acid sulfuric environment.
• Efflorescence formation occurred on the surface of concrete. This suggests the sulfate attack existence in concrete.
• In spite of elapsing near 200 days of exposure, the specimens not only did not lose their weight, but also gain weight. This is attributed to completion of hydration reaction and also filling the pores with the products of sulfate attack. The specimens contained metakaolin showed more weight gain.
• The specimens contained zeolite had the greatest amount of surface sulfate. However, the sulfate in depth of specimen is least.

REFERENCES


