INVESTIGATION ON EXPANSION OF MORTARS CONTAINING TUFF NATURAL POZZOLAN DUE TO SULFATE ATTACK

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ABSTRACT

Sulfate attack and its effects are important from both scientific and industrial viewpoints. It is perceived that cements containing pozzolan have better performance in sulfate solutions, since the pozzolanic reactions reduce the quantity of Calcium hydroxide and increase Calcium silicate hydrate. This paper investigates the physical/mechanical properties of concretes made by blended cement containing Tuff natural pozzolan, and Portland cement. The microstructure of mortars under sulfate attack is studied using SEM analysis and reaction products are characterized using EDS analysis.

The results suggest that, contrary to previous opinions, mortars containing pozzolan show more expansion and unsatisfactory performance in sulfate solution.

Keywords: Sulfate attack; Portland pozzolan cement; Natural pozzolan; SEM analysis

1. INTRODUCTION

External sulfate attack, first identified by USBR in 1908, is a durability problem associated with concrete [1]. Heretofore, numerous laboratory and field studies on deterioration of concrete due to sulfate attack have been performed [2-5].

Sulfate attack often is discussed in terms of reaction between cement hydrates and soluble sulfates such as Sodium, Magnesium and Ammonium sulfates, where their reaction with hydrated cement paste leads to expansion, cracking, spalling and loss of strength. Laboratory studies on sulfate attack have demonstrated the importance of physical factors, viz. porosity, micro cracking and type of cation of sulfate solution [6].

Reaction between Magnesium sulfate and concrete may result in production of Mg-containing hydrates (e.g. M-S-H gel) as well as gypsum and thaumasite. Sodium sulfate may cause deterioration of concrete by the reaction of $\text{SO}_4^{2-}$ ions. Gypsum formation reduces the cohesion, stiffness and strength of the hydrated cement paste [2].

The main factors influencing sulfate attack are [7]:
- $\text{C}_3\text{A}$ content; for cements with 5-8% of $\text{C}_3\text{A}$, sulfate attack is maximum since they contain mostly alumina in the form of monosulfate.

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- C₃S/C₂S ratio; cements containing higher C₃S content, produce significantly higher quantities of Calcium hydroxide upon hydration which may directly react with sulfate ions to produce gypsum.

Recently, owing to ecological, economical and diversified product quality concerns, there has been a growing trend towards using supplementary cementing materials (whether natural, waste or by-products) in the production of composite cements [9-11].

Pozzolans reduce not only the permeability but also the C₃A amount if they are a partial replacement of cement. Moreover, pozzolanic cements, generally reduce the quantity of Calcium hydroxide (CH) due to the pozzolanic reactions [12].

The major hydration product affecting the durability performance of Portland cement pastes, mortars and concretes is the easily soluble Calcium hydroxide. However, this phase can be changed into the relatively insoluble Calcium silicate hydrate phase. This has been achieved by replacement of Portland cement with mineral admixtures such as slag, fly ash, silica fume, and natural pozzolan [13]. Therefore, it is expected that concretes containing pozzolan perform better than control specimens in sulfate solution. Many researches on the performance of concretes containing pozzolan in sulfate solutions have been performed [14-18].

This treatment deals with the properties of mortars and concretes made by Portland pozzolan cement containing about 25% Tuff natural pozzolan under sulfate solution exposure. Results are compared to control specimens containing type II Portland cement. Also microstructure of specimens, after removal of sulfate solution, is studied using SEM-EDS technique.

2. EXPERIMENTS

In the following sections a brief description of the testing program is presented.

2.1 Materials

Aggregates
Crushed gravel and sand were used as coarse and fine aggregates respectively. The aggregates properties are shown in Table 1. Figures 1 and 2 show the particle size distribution of aggregates.

<table>
<thead>
<tr>
<th>Type of aggregate</th>
<th>Specific gravity (gr/cm³)</th>
<th>Absorption (%)</th>
<th>Fineness modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine aggregates</td>
<td>2.53</td>
<td>2.60</td>
<td>2.7</td>
</tr>
<tr>
<td>Coarse aggregates</td>
<td>2.56</td>
<td>1.46</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Tuff natural pozzolan
The Tuff natural pozzolan was used as supplementary cementing material. The chemical composition and physical properties of this pozzolan is presented in Table 2.

Cement
Type II Portland cement of Abyek Cement Manufacturing Co. (Iran), and Portland pozzolan cement with 25% Tuff natural pozzolan replacement were used in this investigation. The chemical composition and physical properties of these cements are shown in Table 2.
### Table 2. Chemical compositions and physical properties of cements and pozzolan

<table>
<thead>
<tr>
<th>Components</th>
<th>Type II cement</th>
<th>Tuff natural pozzolan</th>
<th>Portland pozzolan cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.82</td>
<td>61.38</td>
<td>31.12</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.98</td>
<td>12.54</td>
<td>6.87</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.57</td>
<td>4.23</td>
<td>3.61</td>
</tr>
<tr>
<td>MgO</td>
<td>2.79</td>
<td>0.55</td>
<td>2.35</td>
</tr>
<tr>
<td>CaO</td>
<td>62.84</td>
<td>5.50</td>
<td>47.82</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.24</td>
<td>0.11</td>
<td>1.72</td>
</tr>
<tr>
<td>Na₂O+0.658 K₂O</td>
<td>1.03</td>
<td>---</td>
<td>1.02</td>
</tr>
<tr>
<td>C₃S</td>
<td>52.59</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C₂S</td>
<td>20.03</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C₃A</td>
<td>7.16</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>1.85</td>
<td>2.85</td>
<td>2.11</td>
</tr>
<tr>
<td>Blaine (m²/kg)</td>
<td>3034</td>
<td>5980</td>
<td>3785</td>
</tr>
<tr>
<td>Remained on 90 micron sieve (%)</td>
<td>3.52</td>
<td>2.91</td>
<td>3.38</td>
</tr>
<tr>
<td>Autoclave expansion (%)</td>
<td>0.27</td>
<td>---</td>
<td>0.13</td>
</tr>
<tr>
<td>Water percentage</td>
<td>25</td>
<td>---</td>
<td>28</td>
</tr>
<tr>
<td>Initial setting time (min.)</td>
<td>162</td>
<td>---</td>
<td>163</td>
</tr>
<tr>
<td>Final setting time (min.)</td>
<td>224</td>
<td>---</td>
<td>228</td>
</tr>
<tr>
<td>Compressive strength, 3 days, (Kg/cm²)</td>
<td>223</td>
<td>---</td>
<td>204</td>
</tr>
<tr>
<td>Compressive strength, 7 days, (Kg/cm²)</td>
<td>316</td>
<td>---</td>
<td>297</td>
</tr>
<tr>
<td>Compressive strength, 28 days, (Kg/cm²)</td>
<td>410</td>
<td>---</td>
<td>408</td>
</tr>
</tbody>
</table>

#### 2.2 Tests
a) Compressive strength; measured based on EN 12390-3.
b) Depth of penetration of water under pressure; determined based on EN 12390-8.
c) Length change due to sulfate solution exposure; based on modified ASTM C1012.
d) SEM-EDS Analysis; this analysis was conducted using a CAMBRIDGE 1990-S360 instrument.
2.3 Concrete mixtures
Mixture proportions of control samples (C) and Portland pozzolan samples (P) are summarized in Table 3. Physical properties of fresh concrete are shown in Table 4.

Table 3. Concrete mixture proportions

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Cement</th>
<th>w/cm</th>
<th>Water (kg/m³)</th>
<th>Cement (kg/m³)</th>
<th>Fine aggregates (kg/m³)</th>
<th>Coarse aggregates (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Type II</td>
<td>0.457</td>
<td>160</td>
<td>350</td>
<td>961</td>
<td>853</td>
</tr>
<tr>
<td>P</td>
<td>Portland pozzolan</td>
<td>0.457</td>
<td>160</td>
<td>350</td>
<td>961</td>
<td>853</td>
</tr>
</tbody>
</table>

Table 4. Fresh concrete properties

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Slump (cm)</th>
<th>Density (kg/m³)</th>
<th>Temperature (°C)</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5</td>
<td>2353</td>
<td>29</td>
<td>2.8</td>
</tr>
<tr>
<td>P</td>
<td>5.5</td>
<td>2342</td>
<td>29</td>
<td>2.6</td>
</tr>
</tbody>
</table>

2.4 Curing of specimens
After mixing, concrete specimens were cast into the moulds as specified in EN 12390-2. The control specimens were kept under laboratory conditions for a day, then removed and transferred to the curing basin.

2.5 Mortar mixtures
The mixture proportions of mortar samples are summarized in Table 5. Note that CM stands for the control mortar and PM represents the Portland pozzolan mortar.

Table 5. Mortar mixture proportions

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Cement</th>
<th>w/cm</th>
<th>Water (gr)</th>
<th>Cement (gr)</th>
<th>Fine aggregates (gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>Type II</td>
<td>0.485</td>
<td>1024</td>
<td>2110</td>
<td>5805</td>
</tr>
<tr>
<td>PM</td>
<td>Portland pozzolan</td>
<td>0.485</td>
<td>1024</td>
<td>2110</td>
<td>5805</td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

3.1 Compressive strength
Concrete cubes, 150mm, are used for compressive strength determination. Figure 3 illustrates the results for specimens which are tested in different ages of 7, 28, 42, 90 and 180 days.

![Compressive strength of concrete versus age](image)

An increasing trend of compressive strength is observed for both specimens. At the ages of 28 and 42 days, the compressive strength of P and C specimens are almost equal. Therefore the authors postulate that, Tuff natural pozzolan could be a good choice for partial replacement of Portland cement, since it has negligible effect in decreasing compressive strength yet considerably reduces costs.

3.2 Depth of water penetration test
Tests were conducted on 150 mm cubes at the ages of 28, 56 and 90 days. Results are given in Figure 4. Depth of water penetration into P was lower than C at the age of 28 days, see Figure 4. Albeit at 56 and 90 days, the depth of water penetration into both specimens considerably decreases. At the age of 90 days, the depth of water penetration for P specimens decreased to 50% of water penetration into C specimens. This is attributed to post reactions of natural pozzolans and the resulting filling of porosities by the reaction products.

3.3 Sulfate solution exposure effects
In this test 6 bars (25×25×285mm) and 21 cubes (50mm) were produced with mortars containing Portland cement and Portland pozzolan cement. They were covered with glass to be watertight and placed in a curing tank in water at about 35°C for 24 h. Then they were removed and inserted to 25°C limewater. Two cubic specimens were broken in compression. When the mean strength of these cubes reached to 20 MPa or more, the bars were removed from limewater and placed in sulfate solution. Simultaneously, the concrete cubes for
compressive strength test were prepared and immersed in the sulfate solution.

![Figure 4. Depth of water penetration of concrete versus age](image)

The length change of CM and PM mortars, due to sulfate solution exposure, were determined based on ASTM C1012-02. The results are illustrated in Figure 5. As seen the performance of CM and PM samples are same at early ages, but the samples containing pozzolan have higher expansion at later ages.

![Figure 5. Trend of expansion of mortars due to sulfate solution exposure versus age](image)

The results of compressive strength for samples immersed in sulfate solution are illustrated in Figure 6. The compressive strength increases until 42 days for both C and P specimens. Thereafter, it decreases especially at 180 days of immersion. Besides, the
decreasing rate of P samples is higher than C samples, which confirms the length expansion results.

![Graph showing compressive strength of mortars due to sulfate attack in different ages](image)

**Figure 6.** Compressive strength of mortars due to sulfate attack in different ages

![Image of mortar bars after removal of sulfate solution](image)

**Figure 7.** Image of mortar bars after removal of sulfate solution

Figure 7 depicts the mortar bars after removal from sulfate solution. Evidently the PM specimen is curved because of expansion. Also, some PM specimens had been broken as a result of excessive expansion. This expansion is attributed to the products of reaction between cement with sulfate ions which are massive.
The Scanning Electron Microscope (SEM) equipped with EDS analysis was used for microstructure study of specimens. Figure 8 shows the SEM image of specimen CM. The demarcated areas, i.e. A and B, were evaluated using EDS analysis presented in Figure 9. The relatively flat area, A, in Figure 8 is probably $CH$ crystals whereas region B must be Calcium silicate hydrate ($CSH$) crystals.

![SEM image of control specimen after removal of sulfate solution](image)

*Figure 8. SEM image of control specimen after removal of sulfate solution*

![EDS spectra obtained from pointed areas in Figure 8](image)

*Figure 9. EDS spectra obtained from pointed areas in Figure 8*

The SEM image of PM mortar is shown in Figure 10. The discerned, C and D, were characterized using EDS analysis, Figure 11. Similar to CM specimens, regions C and D are presumably $CSH$ crystals and $CH$ crystals, respectively.
Figure 10. SEM image of specimen containing pozzolan after removal of sulfate solution

Figure 11. EDS spectra obtained from pointed areas (C and D) in Figure 10

Figure 12 illustrates region E; pointed to in Figure 10. This image is prepared at higher magnification to characterize the mortar’s crystals formation. This picture shows formation of ettringite crystals (needles) and gypsum (blades) in a mortar exposed to sulfate solution. It is clear that ettringite has been formed by degradation/deterioration of gypsum crystals as a result of sulfate solution reaction.

Ettringite crystals were formed at earlier ages in the mortars containing pozzolan, compared to control mortars. For the control specimens, all areas of the cement matrix have cured simultaneously, hence crystal growth has occurred uniformly. However, at the same time in the specimens containing pozzolan, there are areas which are not hydrated completely. That is to say, these specimens are heterogeneous owing to the presence of non-reacted areas in hydrated cement matrix. These areas can act as defects in the cement matrix.
and cause the formation of gypsum and ettringite in the sulfate solution. These findings confirm the results of Colak's research [13] and they are in contrary to previous opinions found by [6, 19-20].

![SEM image of produced ettringite on the surface of mortar containing pozzolan (area of E on the Figure 10)](image)

Figure 12. SEM image of produced ettringite on the surface of mortar containing pozzolan (area of E on the Figure 10)

Based on the foregoing results, the increasing trend of strength at early ages can be attributed to the filling of concrete's porosities (especially specimens containing pozzolan) by ettringite formations which strengthen the specimens. Due to slow rate of hydration in concretes containing natural pozzolan, they are degraded by sulfate attack in early ages. The existing pores in the cement matrix are filled by reaction products and cause improvements in compressive strength. Since the volume of reaction products exceed the pores’ volume, micro cracks develop in the cement matrix which in turn reduces the compressive strength.

4. CONCLUSION

The paper presented briefly the findings of a testing program concerning sulfate solution attack. The results imply that partial replacement of type II Portland cement, with about 25% Tuff natural pozzolan had negligible effect on the compressive strength. However, this replacement led to considerable improvement in the water penetration.

Samples containing pozzolan show weaker performance in the sulfate solution in comparison to control samples. Also, the samples containing pozzolan show a higher decreasing rate of compressive strength with higher expansion.

Previous researches had alluded to improvements in the durability of concretes containing pozzolan in sulfate solutions. The current research, predicated on compressive
strength tests after sulfate solution exposure, sulfate expansion and SEM-EDS analysis, manifested that ettringate is developed in the concretes containing pozzolan which results in unsatisfactory performance.

REFERENCES

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