USE OF XRD PATTERNS TO EVALUATE COMpressive STRENGTH OF STABILIZED AGGREGATES

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ABSTRACT

A laboratory study was undertaken to investigate the performance of Class C fly ash-stabilized aggregate bases. Two commonly used aggregates in Oklahoma: (1) Meridian, a limestone aggregate, and (2) Hanson, a rhyolite aggregate, were utilized in this study. Cylindrical specimens were compacted and cured for 1 hour, 3, 28, and 90 days prior to unconfined compressive strength (UCS), X-ray diffraction, and scanning electron microscopy tests. Results show that the UCS of both stabilized aggregates increases with curing time. The Meridian specimens have higher UCS than the corresponding Hanson specimens. The reference intensity ratio (RIR) method was employed to identify and quantify the mass percent of minerals and cementitious compounds in the mixtures. Results show the formation of cementitious compounds such as ettringite, gismondine, straetlingite, and tobermorite, among others, which are responsible for increased UCS. In this study, the sum of all the cementitious compounds (SCC) showed the same qualitatively trend as the UCS trend with curing time. Finally, the UCS values correlate fairly well with the SCC, and, the SEM micrographs show the same trend as the XRD where the intensity of crystal formation is lower in the Hanson specimens than the Meridian.

INTRODUCTION

Class C fly ash (CFA) has been widely used in stabilization pavement applications. It mainly consists of mixing fly ash with aggregate or soil. In the presence of water, these materials (CFA) react with the fine particles to form cementitious compounds that are responsible for the enhancement of engineering properties such as strength and stiffness. Several studies have been conducted in the past to evaluate the performance of CFA-stabilized aggregates or soils in pavement construction. Khoury [1] evaluated the performance of CFA-stabilized aggregate base. Results showed that resilient modulus increased with the percent CFA and curing time. In that study, no laboratory tests were performed to observe the micro-structural developments of the cementitious products responsible for such behavior. Lav and Lav [2] studied the micro-structural development of stabilized fly ash as a pavement base material. Unstabilized (plain fly ash) and stabilized specimens (with cement or lime) were prepared and examined with X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), thermal analysis (TA), and scanning electron microscopy (SEM) to identify the chemical and phase composition and micro-structural development. Cylindrical specimens were also prepared for identifying the variation in their strengths with curing time. The increase in strength of the stabilized specimens with curing time, and the difference between cement and lime-stabilized specimens were justified using the aforementioned tests. This study [2] highlighted the importance of XRF, XRD, SEM, and TA to explain the mechanisms associated with stabilization.
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These and other studies indicate a need for additional research to understand the cementitious reactions associated with the stabilization of aggregate bases. The experimental study reported herein is an attempt to address this need. Specifically, this paper presents the unconfined compressive strength (UCS) of two types of aggregates stabilized with CFA. Results from the XRD and SEM tests are also presented to rationalize the effect of curing time and aggregate mineralogy on UCS. Efforts are made to quantify the cementitious compounds associated with stabilization by utilizing the reference intensity ratio (RIR) method.

MATERIALS AND SPECIMEN PREPARATION

Two commonly used aggregate bases in Oklahoma: (1) Meridian, a limestone aggregate; and (2) Hanson, a rhyolite aggregate, were utilized in this study. Bulk aggregates were collected from two different quarries in Oklahoma, one for each aggregate type. The mineralogical and physical properties of the aggregates are summarized in Table 1. Class C fly ash (CFA) was obtained from Boral Materials Technologies, Oologah, Oklahoma. It contains approximately 62.9% of SiO₂ (Silica) + Al₂O₃ (Aluminum) + Fe₂O₃ (Iron Oxide) compounds (SAF), with 38% representing Silica (SiO₂). The total Calcium Oxide (CaO) content is approximately 25.1%. In addition, CFA has an average specific gravity of 2.69, a loss on ignition (LOI) of 0.23%, and a moisture content of 0.33%.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Meridian*</th>
<th>Hanson**</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>3.00</td>
<td>67</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>---</td>
<td>13</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>---</td>
<td>10</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>91.3</td>
<td>---</td>
</tr>
<tr>
<td>CaO</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>MgO</td>
<td>0.7-1.2</td>
<td>---</td>
</tr>
<tr>
<td>Loss on ignition (LOI)</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

A total of 24 Harvard miniature specimens were prepared and tested for UCS, XRD, and SEM. Materials passing No. 40 sieve were mixed with 10% CFA, and then compacted at near optimum moisture content (OMC) and approximately 98% maximum dry density (MDD). The compacted stabilized specimens were cured for 1 hour, 3, 28, and 90 days in a desiccator at room temperature of approximately 21°C (70°F) and a relative humidity of approximately 90%.

UCS, XRD, AND SEM TESTS

The unconfined compressive strength (UCS) tests were performed on stabilized specimens. Specimens were loaded at a constant axial strain of 0.0282 in/min. A dial gauge was used to measure the vertical deformation, and a load ring to measure the load.

The X-ray diffraction (XRD) tests were performed using a Rigaku D/Max X-ray diffractometer with bragg-brentano parafocusing geometry, a diffracted beam monochromator, and a conventional copper target x-ray tube set to 40 KV and 30 mA. Data obtained by the diffractometer were analyzed with Jade 3.1, an X-ray powder diffraction analytical software,
produced by the Materials Data, Inc. Tests were conducted on a small portion of duplicate specimens after the completion of the UCS test. The material was oven dried for approximately 24 hours, grounded with a mortar and pestle, and then sieved through a No. 200 sieve. The materials passing No. 200 sieve were placed on a specimen holder prior to testing.

The SEM technique was employed to qualitatively identify the micro-structural developments in the matrix of the stabilized mix. Tiny pieces were collected from one of UCS-specimen replicates and then oven dried for approximately 24 hours. Two tiny pieces were mounted on a copper specimen holder and then coated with a thin layer of gold palladium to provide surface conductivity. Technics sputter coater operating under a vacuum of 40 millitors and 10 mA current was used for this purpose. The coated pieces were placed in a JEOL JSM 880 scanning electron microscope operating at 15 kV. The micrographs were taken using EDS2000. Similar to XRD, the SEM examination was performed on a tiny portion of the specimen, but it is believed to be representative of the reaction process of the additive-aggregate mixture.

PRESENTATION AND DISCUSSION OF RESULTS

The UCS values of the stabilized specimens are shown in Figure 1, as a function of curing time. The unconfined compressive strength (UCS) for both Meridian and Hanson specimens increased with curing time. The UCS of Meridian specimens increased approximately 25% and 70% as the curing time increased from 1hr to 3 and 28 days, respectively.

The percentage increase (70%) as the curing time increases from 1hour to 28 days is higher than the percentage increase (5%) in UCS values as curing time increases from 28 to 90 days. It is an indication that the 28-day curing time can be considered sufficient criterion for a significant strength gain of CFA-stabilized aggregate base; curing periods longer than 28 days did not cause any significant increase in UCS values. From Figure 1, one can also observe that Meridian specimens have higher UCS values than the corresponding values for the Hanson specimens. Thus, it is advanced that the aggregate mineralogy influences the unconfined compressive strength values. One of the contributing factors in this regard is the amount of SAF compound in an aggregate. Meridian with the highest UCS values has the highest SAF and CaCO₃ compounds.
(approximately 94%), while Hanson aggregate has a slightly lower amounts (approximately 90%).

Efforts were made to explain such behavior in light of the XRD and SEM test results. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) tests were performed on stabilized specimens to justify and explain the aforementioned experimental observations. The diffractograms of the stabilized specimens are presented in Figures 2 and 3.

The Reference Intensity Ratio (RIR) method was used to analyze the data, rather than the intensity of the peak channel alone. The RIR is a constant relating the X-ray scattering power of a phase to that of the internal standard [3-5]. The RIR method consists of fitting the raw data to a specific profile shape, eliminating the contribution of overlapping peaks, and subtracting background. This method is a quantitative method [3-5] that calculates the weight % in the least-square fit of the identified minerals and compounds. However, the results are only as good as the RIR values can be. Any profile error due to intensity (%) and positional mismatches in individual powder diffraction file (PDF) lines also influence jeopardize the accuracy of the final numbers [5]. Results from the RIR method, with a least square error ranging between 30% and 50%, reveal the following characteristic trends for the tested specimens:

1) Calcite (CaCO₃) are the predominant minerals in Meridian mixes. In Hanson, however, quartz (SiO₂) is the predominant component in the presence of clay minerals such as Illite, Zeolite, and Beotite. The aggregates (limestone and rhyolite) and partly the stabilizing agents are the main sources of these minerals.

2) Ettringite was found in all specimens. Ettringite is a calcium aluminum sulfate hydrate (CASH) type mineral. It is responsible for the early strength gain.

3) Also, gismondine was detected in all specimens; however, the intensity is higher in 28- and 90-day cured specimen than in 1-hour and 3-day cured specimens. It is believed that gismondine is responsible for long-term strength performance of the stabilized specimens.

4) A trace of (C₃A·H₆) (3CaO·Al₂O₃·6H₂O) was depicted in all specimens.

5) Saitoetlingite (C₂S·AH₈) and Tobermorite were only found in Meridian specimens.
In this study, it was decided to correlate the unconfined compressive strength with the sum of the cementing compounds (SCC) (i.e., ettringite, gismondine, C₃AH₆, strætlingite, and tobermorite), since no specific trend was observed between the UCS values and each cementitious product. Figure 4 shows the variation of SCC values with curing time.

SCC increased with curing time and has the same qualitative trend as UCS. Correlation between UCS values and SCC is shown in Figure 5. The unconfined compressive strengths increased approximately linearly with SCC, with a relatively high R² value (0.84). Such a correlation would be extremely helpful in better understanding and rationalizing the mechanisms associated with stabilization. It would also be helpful in evaluating the durability of stabilized aggregate bases, which is beyond the scope of this study. Livingston et al. (1998) have previously used the XRD as a quantitative method to observe the durability of bricks.
The SEM tests were performed to observe the micro-structural changes in the matrix of the stabilized specimens and to visually examine the resulting hydration products. The SEM micrographs presented in Figures 6 and 7 show the evidence of crystal formation in the matrix aggregates. It is evident that the degree of crystal formation and paste surrounding the particles varies with curing and differ from one aggregate to another. The micrographs show that Meridian stabilized specimens exhibit a higher intensity crystals than Hanson stabilized specimens. These experimental observations are consistent with the XRD trends.

CONCLUDING REMARKS

This study was undertaken to investigate the UCS of aggregate bases stabilized with Class C fly ash. Results showed that the UCS increased with curing time. The percent increase in UCS with increasing curing time from 1 hour to 28 days was higher than the corresponding percent increase in UCS for increased curing time from 28 to 90 days. It was also found that Meridian, a limestone aggregate, had higher UCS than the UCS of the Hanson aggregate which is a rhyolite type aggregate. It is an indication that aggregate mineralogy has an influence on the increase in UCS due to stabilization. The RIR method was used to identify the cementing compounds in the stabilized specimens. Cementing compounds such as ettringite, gismondine and tobermorite, among others, were identified and their mass percent varied from one stabilized specimens to another. Correlations between the sum of cementing compounds (SCC) and UCS values showed a fairly consistent trend. The UCS values increased approximately linearly with SCC. The micro-structural development of crystals in the mixtures reveals the same trend as the XRD patterns. The intensity of crystals was lower in Hanson than in Meridian specimens.

Findings from this study demonstrate a need for additional research to implement the quantitative X-ray diffraction method to fully understand the extent of cementitious reactions occurring in the stabilization process. Additional studies using quantitative approaches such as RIR to determine the cementing compound developments with time would be helpful in better understanding the chemical reactions and their short- and long-term implications on stabilization process.

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REFERENCES