Pozzolanic reactions between natural and artificial aggregate and the concrete matrix

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A concrete mix containing 3 different types of aggregate was prepared in order to study the pozzolanic reactions between the aggregates and the cement matrix. Sandstone aggregate, manufactured aggregate made from coal fly ash and manufactured lightweight aggregate made from expanding shale were used. The fly ash aggregate, expanding shale aggregate, and sandstone aggregate contain glass phases of 80%, 60% and 0% respectively.

Pozzolanic reactions between dissolved elements from glass and calcium from portlandite occurred. Hydroxyl ions break down the silica in the glass, which in turn react with the calcium in the portlandite to form CSH paste. This reaction increases the bond strength between the aggregate and the cement matrix.

KEYWORDS; concrete, aggregate, glass, pozzolanic reaction, portlandite

1. Introduction

An artificial aggregate made from coal fly ash was produced by a rotary kiln. The pores in the aggregate are closed and sphere shaped, which correspond to greater strength and lower water absorption than the conventional lightweight aggregates on the market. Since the aggregate is composed mainly of a glass phase, pozzolanic reactions surrounding the aggregate are expected. In this study, a concrete mix containing sandstone aggregate, artificial lightweight aggregate made from coal fly ash and lightweight aggregate made from expanding shale were mixed to study the physical change of the aggregate surface. Abbreviations referring to the aggregates used are listed in Table 1.
Studies concerning the pozzolanic reaction on the surface of coarse aggregate have yet to be undertaken. Pozzolanic reactions between the concrete matrix and the coarse aggregate would lead to an increase in strength of the concrete because of the increased bond strength between the concrete and the aggregate.

Table 1 Abbreviations used in this study

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Coal fly ash aggregate</td>
<td>FA</td>
</tr>
<tr>
<td>Conventional lightweight aggregate</td>
<td>LA</td>
</tr>
<tr>
<td>Crushed sandstone aggregate</td>
<td>NA</td>
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2. Aggregates and Experiments

2.1 Aggregate made from fly ash

There are two types of carbonaceous fragments in the fly ash. One is free from other inorganic particles or intermixed with inorganic material. The other is trapped in a glass sphere (cenosphere). The trapped carbonaceous material is combustible at high temperatures in oxygen containing environments. When the trapped carbonaceous fragments in aggregate particle remain at the firing process, the aggregate expands heterogeneously as shown in Fig.1 (a). This aggregate is weak and water absorbent. However, the aggregate expands uniformly, as shown in Fig1 (b), by the expansion of the trapped carbonaceous matter when the free fragment have already burned before the expansion process. This process was described by Imai et al\(^1\), and is shown in Fig.2.

This aggregate has higher strength and lower water absorption than the conventional manufactured lightweight aggregate\(^1\). The fly ash aggregate used in this study was fired in a rotary kiln to cause the latter expansion mechanism. A schematic of the production process is shown in Fig.3. “Refractory powder” is used to prevent adhesion of the aggregate particles at elevated temperatures. The properties of this aggregate are listed in Table 2. The strength is comparable to that of natural aggregate.

Glass contents of FA and LA were about 80-90% and 60-70% respectively determined by semi-quantitative analysis of x-ray diffraction.
Fig. 1 Two types of bloating by two types of carbonaceous matter.

Fig. 2 Microscopic photo of fly ash particles at elevated temperatures. (Compare the each arrow at different temperature)

Fig. 3 Production process of fly ash aggregate
2.2 Other aggregates

Manufactured lightweight aggregate (LA) and crushed sandstone (NA) were used. Dry density and water absorption of the aggregates are listed in Table 3.

Though the water absorption is commonly expressed as a gravimetric value, a volumetric value is more suitable to compare the aggregates of different density. Because the density of water is almost one, (g/100mL) means the volume of water-absorbable space in 100mL aggregate.

Table 2 Properties of the fly ash aggregate (FA)

<table>
<thead>
<tr>
<th>Property</th>
<th>FA</th>
<th>LA</th>
<th>NA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum size (mm)</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry density (g/cm³)</td>
<td>1.7~1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water absorption (%) after 24 hours in water</td>
<td>2.0~2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abrasion (%)</td>
<td>13.2~20.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Durability soundness (%)</td>
<td>0.0~0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unit weight (t/m³)</td>
<td>1.12~1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid volume percentage (%)</td>
<td>62~64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crushing load (kN, average)</td>
<td>Diameter(5~10mm)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diameter (10~15mm)</td>
<td>2.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Properties of coarse aggregates used for concrete

<table>
<thead>
<tr>
<th>Property</th>
<th>FA</th>
<th>LA</th>
<th>NA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.83</td>
<td>1.31</td>
<td>2.72</td>
</tr>
<tr>
<td>Water absorption (mass %)</td>
<td>2.60</td>
<td>28.0</td>
<td>0.83</td>
</tr>
<tr>
<td>Water absorption (g/100mL)</td>
<td>4.76</td>
<td>36.7</td>
<td>2.26</td>
</tr>
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</table>

2.3 Mixing conditions for concrete

20% of fly ash was substituted for cement. Ratios of water to binder (cement + fly ash) were 30% and 55%. The same volume ratios of the three aggregates were added to the paste simultaneously to ensure the same paste aggregate interaction for each of the aggregates. The mixture was poured into 40 × 40 × 160 mm molds and studied at 7, 28 and 182 days.

2.4 Methods for evaluation

Optical microscopy and x-ray microanalysis (XMA) were the methods of analysis.
used to investigate the pozzolanic reaction. The hydration process was stopped using acetone at 7, 28, and 182 days and then cut in half, as shown in Fig.4. One side was used for XMA and the other for microscopy.

![Fig.4 Cut specimen. The square is analyzed area. The fly ash aggregates are circular, the conventional lightweight aggregates are black and the others crushed sandstones.](image)

3. Experimental Results

3.1 Microscopy

Microscopic photos by polarized light are shown in Fig.5. The FA is mostly composed of glass phases evidenced by the fact that FA is almost dark at the crossed Nicol.

Fig.6 shows cracks developing in the matrix and the lightweight aggregate. This is an indication of the strength of conventional manufactured lightweight aggregate. These cracks did not occur in the fly ash aggregate and natural aggregate.
3.2 XMA results

Fig. 7 and Fig. 8 show concentrations of CaO with different gradients. In all cases, the XMA maps show high calcium local concentrations in the matrix. These are alite (Ca$_3$SiO$_5$) and belite (Ca$_2$SiO$_4$).

High calcium zones appear at the paste-aggregate interfaces. This high calcium
zone, shown in Fig.7 and Fig.8, is composed of portlandite (Ca(OH)$_2$). The portlandite zone for the natural aggregate is the thickest and there is no significant change in the thickness of the portlandite zone with curing time. However, the thickness of the portlandite zone for FA and LA decreases significantly with time for the 55% W/B sample.

Fig.9 to Fig.11 show similar patterns related to type of aggregate and the thickness of the portlandite zone. Changes in concentration with curing time for 33% W/B are not as distinct. This can be explained by lower W/B corresponds to lower porosity or ion migration/diffusion. For W/B=55%, the ion migration is much more significant.
Fig. 7 CaO concentration around of the aggregate
Fig. 8 CaO concentration with different gradient of Fig. 6
Fig. 9 CaO/SiO$_2$ concentration around the aggregate
Fig. 10 Na$_2$O concentration around the aggregate
Fig. 11 Al₂O₃ concentration around the aggregate
4. Discussion

Glass phases are one of the materials that are susceptible to pozzolanic reactions. The pozzolanic reaction occurs at the surface of FA and LA because of the high amounts of glass phases. The primary reaction of any pozzolanic material is an attack on SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} framework by OH\textsuperscript{−} ions\textsuperscript{2}. Silica and alumina species broken from the glass framework react with Ca(OH)\textsubscript{2} and form CSH CASH phases and minerals. Because the glass phase is easily attacked by OH\textsuperscript{−} ions, the pozzolanic reaction is expected occur around FA and LA and some minerals.

Fig.9 show that CaO/SiO\textsubscript{2} of FA/LA at 55% W/B decreased with time. And Fig.11 shows an increase of SiO\textsubscript{2}.

4.1 Evidence of pozzolanic reaction

For W/B=55% concrete, element-concentrations were found to change with time around the aggregate particles. Moreover, size of the portlandite zone around FA and LA decreased with time. Whereas the portlandite zone around NA experienced no significant changes. The decrease of portlandite indicates that calcium ion could be reacting with silica/alumina dissolved from FA/LA. Alkali Silica reaction is considered unlikely based on the fact that the portlandite zone around the natural aggregate remains unchanged after 180 days. These reactions would be pozzolanic reactions.

The zone of portlandite on aggregate is called “transition zone”. Hanehara et al.\textsuperscript{3} analyzed relation between the thickness of transition zone and concrete strength. They found an inverse relation to the thickness and the strength. The decrease of portlandite zone thickness around FA/NA will increase the concrete strength.

For LA, an increase in concrete strength would not be expected based on the weakness of the aggregate. However the use of fly ash manufactured lightweight aggregate in concrete will correspond to an increase the strength. Long term compressive strength tests will need to be performed in order to confirm the findings of this report.

The strength of the new fly ash manufactured lightweight aggregate make it an attractive product for the near future.

4.2 Effect of W/B ratio to pozzolanic reaction

Low W/B concrete didn’t show a clear change of concentrations, or phase changes. This means that pozzolanic reaction wasn’t significant 182 days. However,
diffusion/migration of elements occurred at the higher W/B concrete. Similar trends were reported by Yamamoto et al. They mentioned that pozzolanic reaction is controlled by diffusion kinetics and that low water/cement matrix constrains the diffusion.

5. Conclusion

A concrete mix containing 3 different types of aggregate was prepared. The surface of each aggregate was evaluated by use of microscope and X-ray micro analyzer. The conclusions are as follows,

1. The portlandite zone on the surface of glass rich aggregate decreases in thickness with curing time. However, the zone on the natural aggregate doesn’t change in thickness.
2. The decrease of portlandite is the result of a reaction between calcium ion and silica/alumina ion dissolved from glass. This is called the pozzolanic reaction.
3. This decrease of portlandite at the aggregate surface corresponds to an increase in the strength of the concrete.
4. Though the thickness of portlandite on the conventional lightweight aggregate decreases, the conventional aggregate does not contribute to an increase in strength of the concrete, because the aggregate is too weak.
5. Since the new aggregate made from fly ash has a compressive strength comparable to natural aggregate, its use will strengthen the concrete.
6. With low water ratio concrete, the pozzolanic reaction did not occur at 182 days because the diffusion kinetic was very small.

References