Quantification of the degree of reaction of alkali activated fly ash by image analysis

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ABSTRACT

Alkali activated fly ash (AAF) is one of the promising cementious materials in recent years. The durability of AAF, which has a significant influence on the service life design and safety, is closely related to its chemical composition and microstructure. In order to better understand the compositional change and microstructure development under different condition, and further evaluate the durability of AAF, the quantification of reaction degree is an important parameter.

In this study, image analysis of backscattered electron (BSE) images was proposed to quantify the reaction degree of alkali activated fly ash. A combination of filters and grey level thresholding was applied to distinguish the boundary between the unreacted FA and the reaction products. Based on the volume fraction of unreacted fly ash, the reaction degree of AAF can be calculated. The results indicate that the reaction degree derived from image analysis is reliable and consistent, which correspond well with the compressive strength of AAF.

Key-words: alkali activated fly ash, reaction degree quantification, image analysis

INTRODUCTION

Alkali activated materials (AAM), also called geopolymers [1-2], are newly promising cementious materials in recent years. By using waste materials and byproducts from industrial process as the raw materials, the production of AAM decreases the CO₂ emission significantly. Fly ash is one of the most common raw materials for AAM.
The durability of alkali activated fly ash (AAF), which has a significant influence on the service life design and safety, is closely related to its chemical composition and microstructure. In order to better understand the compositional change and microstructure development under different condition, and further evaluate the durability of AAF, the quantification of reaction degree is an important parameter.

However, quantification of reaction degree in alkali activated system is challenging. The original fly ash contains a large amount of amorphous phases. Meanwhile, the reaction products are mostly amorphous. It is very difficult to distinguish the reaction products from the original fly ash. In addition, because of the highly alkali and viscosity condition in the alkali solution, the direct detection of reaction is also difficult. Fernández et al. [3-5] reported the reaction degree of alkali activated fly ash can be measured by the chemical attack method. By subjecting the AAF to a 1:20 HCl solution, only the reaction products were dissolved during the process, while the unreacted fly ash remained. However, the effect of the HCl solution on the original fly ash was not mentioned. Similar acid attack method was reported to dissolve considerable part of fly ash in fly ash blended cement system [6]. On the other hand, the image analysis method was widely applied [7-10] to quantify the reaction degree in cement system. Thus, it is also possible to use this method in AAF system to determine the reaction degree.

In this paper, the image analysis of backscattered electron (BSE) images was applied to get the volume portion of unreacted fly ash in alkali activated fly ash system. Based on the original portion of fly ash in the starting mixture, the degree of reaction can be calculated.

**MATERIALS AND EXPERIMENTS**

**Materials**

In this study, the Class F fly ash (according to ASTM classification) obtained in The Netherlands was used to produce alkali activated fly ash. The chemical composition of hereby used fly ash was determined by X-ray fluorescence (XRF) spectrometer, which is shown in Table 1. The alkaline solutions were prepared by mixing sodium hydroxide (analytical grade, >98% purity) with sodium silicate solution (Na₂O: 8.25 wt. %, SiO₂: 27.5 wt. %) and demineralized-water. Three mixture with different content of alkali solutions were prepared, detailed information presented in Table 2.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fla Ash</td>
<td>48.36</td>
<td>31.36</td>
<td>4.44</td>
<td>7.14</td>
<td>1.35</td>
<td>1.64</td>
<td>0.72</td>
<td>1.24</td>
<td>1.9</td>
<td>1.18</td>
</tr>
</tbody>
</table>

**Sample preparation**

Alkali activated fly ash specimens were cast by mixing fly ash with alkaline solutions. The water to fly ash ratio was kept constant at 0.35 (including water in water glass).
Samples were prepared by casting slurry in a plastic bottle, vibrating, and then sealed curing in an oven at 40 °C. At each curing age (7 days and 28 days), the samples were taken out from the oven, crushed by a hammer into small pieces about 1-2 cm³. The reaction of the samples was then stopped by immersing in liquid nitrogen and the specimens were then placed in a freeze-dryer at -28 °C. This quick freezing and drying process at low temperatures allows the remaining alkaline solution transforming into ice microcrystals and removed by sublimation without a large change of the microstructure of AAF.

**Table 2: Compositions in alkali solutions (mol) mixed with 1 kg fly ash**

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂(mol)</th>
<th>Na₂O(mol)</th>
<th>H₂O (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1.5</td>
<td>1</td>
<td>1.5</td>
<td>0.35</td>
</tr>
<tr>
<td>1-1.3</td>
<td>1</td>
<td>1.3</td>
<td>0.35</td>
</tr>
<tr>
<td>1-1</td>
<td>1</td>
<td>1</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The samples have to be prepared carefully, including epoxy impregnation, cutting, grinding and polishing. In order to obtain high quality image, specimens need to be well grinded and polished. To prepare the samples, the surfaces of the specimens were first ground on the middle-speed lap wheel with successively SiC paper for 3 minutes: p320, p500, p800, p1200 and p2400. Then polishing was carried out on a lap wheel with successively finer grades of diamond abrasive cloth: 3, 1 and 0.25 µm. The final polishing was carried out on a low-relief polishing cloth. For each grinding and polishing procedure, ethanol was applied as lubricant. After polishing, the specimens were placed in an ultrasonic bath to remove the dust and diamond particles left on the surface (more details about the sample preparation procedure are as reported in [11, 12]).

For comparison, compressive strength of the specimens were tested at the same age as for image analysis. Specimens were cast in plastic mold 40mm×40mm×40mm, sealed curing in oven at 40 °C.

**Scanning electron microscopy and image analysis**

Backscattered electron (BSE) images of the polished samples were acquired by using Scanning electron microscopy (using environmental SEM (ESEM Philips XL30)). The accelerating voltage of the beam was 15 kV. BSE images generate a specific phase contrast, allowing phases to be identified according to their brightness in the image: those with the higher atomic number being brighter, and that with the lower atomic number is darker. This allows the components of different phases to be discriminated on the basis of the grey level histogram of the image (distribution of the grey levels of all pixels of the image). In this study, the physical size of the reference region of each image is 248 µm in length and 188 µm in width. The magnification is 500× and the image size is 1424 × 968 pixel. Thus the resolution of the image is 0.19 µm. Image analysis was performed on 15 locations randomly selected for each sample to ensure that the results are statistically relevant.
Image analysis was carried by using different filters to the BSE images to get the volume fraction of unreacted fly ash particles based on segmentation methods (the details about the image analysis will be further discussed below).

**DETERMINATION OF REACTION DEGREE**

Backscattered electron imaging provides image contrast as a function of element composition [13]. The grey level of phases in BSE image is proportional to the backscattered coefficient which is related to their average atomic weight and density. Thus, the higher the average atomic number or density the phase has, the brighter it is in the backscattered image [14-15]. Fig.1 presents the representative BSE image of fly ash sample after epoxy in this study. Generally, the morphology of fly ash particles is spherical in BSE images (point 1 in Fig.1). However, irregular morphology of the fly ash particles was also observed in BSE image (point 2 in Fig.1). Further, fly ash particles have different brightness, depending on their chemical composition (point 3 in Fig.1). Therefore, it is difficult to well distinguish the un-reacted fly ash particles in AAF. In this study, by using the image analysis based on applications of different filters to the BSE images and segmentation methods, the un-reacted fly ash particles was well defined and the reaction degree of the AAF was calculated which is described as follows.

![Fig.1 Backscattered electron (BSE) images of fly ash particles used in this study](image_url)

The original BSE image of AAF at 7 days curing age and the corresponding grey level histogram are shown in Fig.2. Because the image was acquired in 8 bits, 256 grey level values are included in the image, ranging from 0 (black) to 255 (white). Typical phases of the AAF can be distinguished: un-reacted fly ash particles bright; reaction products gel light grey; pores black.

The reaction degree of AAF can be determined by measuring the area fraction of the un-reacted fly ash particles in the images. To do this, the area corresponding to the un-reacted fly ash particles needs to be segmented from the image. In the simplest situation,
the segmentation can be directly performed on the basis of the grey level. However, in
the case of AAF, some parts of the fly ash particles and reaction productions will overlap
in the histogram, especially for the Si rich part in the unreacted fly ash particles (circled
in the ESEM images, Fig.2 (a)) and the high density gel. Therefore, it is difficult to
determine the boundary between the un-reacted fly ash particles and reaction products
(Fig.2 (b)). In this study, the segmentation of the un-reacted fly ash particles from the
image was based mainly on the operations by applying area selection tool and
morphological filter. Other image analysis operations (e.g. hole filling) were also applied
to the segmented image to improve the reliability. By using these tools, we can easily
know if all the fly ash particles were selected from direct observation. After all the fly ash
particles were selected, use the delete button to turn the selected image into white. In this
way, the fly ash particles were separated from the image. Fig.3 shows the BSE images
after segmentation and the corresponding grey level histogram. It can be observed from
the grey level histogram (Fig.3 (b)) that after the segmentation, the boundary between the
un-reacted fly ash particles and the reaction products becomes much clearer.

![Fig.2 (a) Original backscattered electron (BSE) images of the AAF at 7 days curing age;
(b) Corresponding grey level histogram](image)

![Fig.3 (a) Resultant backscattered electron (BSE) images of the AAF at 7 days curing age
after segmentation; (b) Corresponding grey level histogram](image)

The ESEM image after the segmentation was then transformed into a binary image with
the un-reacted fly ash particles as white and the rest phases of AAF as black background.
The binary image was then subjected to several 3 × 3 morphological filters (erosions, dilations, closing) and the resultant images (Fig.4) consisted only of the un-reacted fly ash particles. By utilizing the thresholding, the percentage of unreacted fly ash particles is obtained.

![Fig.4 Binary image of the AAF at 7 days curing age](image)

The degree of the reaction of AAF at certain time, \( \alpha(t) \), is calculated from the following equations:

\[
\alpha(t) = (1 - \frac{U_t}{U_0}) \times 100\%
\]

Where \( U_t \) is the volume fraction of unreacted fly ash particles at the age of t (obtained from the image analysis); \( U_0 \) is the initial volume fraction of fly ash particles. The initial volume fraction of fly ash particles is calculated according to the solution/fly ash volume ratio. For specimen 1-1 and the water/fly ash mass ratio 0.35, the volume of the activating solution was measured 0.36 L that mixing with 1 kg fly ash. The density of the fly ash was measured to 2.44 g/cm\(^3\); corresponding to the volume of 0.41 L with respect to 1 kg fly ash. Thus the initial volume fraction of fly ash of 1-1 was 46.75%.

![Fig.5 Degree of reaction and compressive strength over time in AAF, A-Reaction degree, B- Compressive strength](image)
RESULTS

According to the image analysis method described above, the reaction degree of three different activators mixtures (SiO\textsubscript{2}-Na\textsubscript{2}O = 1-1, 1-1.3 and 1-1.5) at different age was obtained and displayed in Fig.5 A. These three mixtures were mainly different in alkali content in the activating solution (1, 1.3 and 1.5 mol/kg fly ash). As shown in Fig.5 A, with more alkali content, the reaction degree is higher both at 7 days and 28 days. The compressive strength of the three mixtures at the curing age of 7 days and 28 days was shown in Fig.5 B. Comparing the results of reaction degree with its compressive strength, specimen with higher reaction degree exhibits higher compressive strength at both curing age. Thus the reaction degree obtained by the image analysis corresponds very well with the compressive strength. However, comparatively large variations were found on the image analysis results, especially for specimen 1-1 at both curing age. That’s mainly because the heterogeneous properties of the fly ash and a low reaction happened for sample 1-1, which cause very locally reaction. Thus, increasing the number of analyzed image was regarded to minimize the variations significantly.

CONCLUSION

In this paper, image analysis of BSE images was proposed to quantify the degree of reaction of alkali activated fly ash. A combination of filters and grey level thresholding was applied to distinguish between the unreacted FA and the reaction products. Based on the volume fraction of unreacted fly ash, the reaction degree of AAF can be obtained. It was found the reaction degree deduced from image analysis gave a reliable and consistent result, which correspond very well with the compressive strength.

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