Study on the reaction degree of calcined coal gangue powder in blended cement by selective solution method

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Abstract
Calcined coal gangue powder was used to partially replace Portland cement (PC) at 10\%, 20\%, 30\%, and 40\% by weight. The water to binder ratio (w/b) of 0.5 was used for all the blended cement paste mixes. The reaction degree of calcined coal gangue powder in calcined coal gangue powder/cement (AC) was determined using a selective dissolution method. It was found that high-volume calcined coal gangue powder pastes underwent a lower degree of reaction of calcined coal gangue powder. The effect of calcined coal gangue powder replacement on the reaction degree of calcined coal gangue powder in AC pastes in later age was less than that of in early age.

Keywords: calcined coal gangue powder; cement paste; hydration; reaction degree

1. Introduction
Coal gangue is waste residue during coal mining and coal washing. Generally, coal gangue comprehensive discharge capacity takes the 15\% - 20\% of the output of raw coal. Statistics according to national state economic & trade commission shows that the annual emission of coal gangue in China is near to one-hundred millions tons \cite{1-2}, which is now amounted to more than 3000 millions tons.

Because of different mineral contents of the coal in different place, the chemical composition is relatively complex, which is about 10 kinds of element probably \cite{3}. The major composition normally is silicon and aluminum. Most of the coal gangue is a clay rock; whose main mineral composition consists of clay mineral, mineral quartz, potassium feldspar, anorthite, siderite, pyrite, and calcite. Previous research shows \cite{4}, the bonding of gel role of fresh coal gangue is very weak, because this kind of coal gangue have steady crystal structure, whose atom, ion, and member etc. are put according to certain law by order, even if its chemical composition is proper and lowly active, however, coal gangue has certain activity after burning. After calcined at a certain temperature, the clay mineral is dewatered and disintegrated, the carbon component is removed with the deteriorative impurity burned out. The crystal is disintegrated and transformed into amorphous non-crystal, which makes the coal gangue active.

The usage of activated coal gangue powder in concrete can lead to many technical advantages \cite{5}. While a number of studies have been conducted on high-performance Metakaolin(MK) concrete or mortars \cite{6}, there have been few studies concerning the hydration progress of MK, or similar MK additives. According to the article \cite{7}, the degree of pozzolanic reaction of MK in these pastes was quantitatively determined using a selective dissolution method. This method has been developed for quantifying the degrees of pozzolanic reactions, which is different from traditional methods for assessing the degree of cement hydration through the determination of nonvolatile water and CH contents. A more quantitative understanding of the hydration process of blended cement with different levels of calcined coal gangue powder is needed.

This paper presents extensive experimental results of a quantitative analysis of the hydration of blended cement pastes with different percentages of calcined coal gangue powder.

2. Experimental

2.1. Materials

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The 52.5R Portland cement produced by Huaxin Cement plant in Hubei Province was used in all the pastes mixtures. Coal gangue powder was obtained from Qitaihe coal mine in Heilongjiang province. The calcining temperature of coal gangue was 820 °C. The surface area of calcined coal gangue powder is 480 m$^2$/kg. The chemical composition characteristics of cement clinker and calcined coal gangue powder are described in Table 1. The mineral composition was calculated by quantitative analysis of XRD. The results were described in Fig. 1.

Table 1. Chemical and physical properties of the cementitious materials

| Chemical composition | Cement clinker | Calcined coal gangue powder |
|----------------------|----------------|-----------------------------|
| SiO$_2$ (%)          | 21.06          | 57.95                       |
| Al$_2$O$_3$ (%)      | 6.04           | 19.02                       |
| Fe$_2$O$_3$ (%)      | 3.63           | 5.32                        |
| CaO (%)              | 63.98          | 3.16                        |
| MgO (%)              | 2.67           | 0.82                        |
| SO$_3$ (%)           | 2.25           | 0.64                        |
| Density              | 3.15           | 2.43                        |

2.2. Preparation of cement pastes

AC pastes were prepared at the w/b ratio of 0.5 which is the quite common value in practice. Calcined coal gangue powder was used as the replacement of cement at the levels of 10%, 20%, 30% and 40% by weight. Plain PC pastes without any calcined coal gangue powder replacement were prepared at the same w/b ratios as that in references. The pastes were mixed in a mechanical mixer, and cast in a 20 mm×20 mm×20 mm steel mould. The steel moulds were removed 24 h after mixing, and the cubes were cured in water at 20±2 °C.

2.3. Determination of non-evaporable water

Wn contents of the hydrated cement pastes were determined to evaluate the degree of hydration.

All the calculations described in this subsection and the following subsections were carried out on the ignited basis (i.e. 1 g of sample was ignited at 950 °C in an electric furnace for 1 h). The loss on ignition (LOI) of the as-received calcined coal gangue powder and cement, and hydrated cement pastes was calculated by Eq(1):

$$\text{LOI(\%)} = 100 \times \frac{\text{as-received weight} - \text{ignited weight}}{\text{ignited weight}}$$

The original fractions of calcined coal gangue powder(a) and cement(c) in an AC paste on an ignited basis were calculated by:

$$a \text{ or } c = \frac{\text{ignited weight of calcined coal gangue powder or cement}}{\text{ignited weight of calcined coal gangue powder + ignited weight of cement}}$$
where the ignited weight of calcined coal gangue powder or cement can be calculated by:

\[
\text{Ignited weight} = \frac{\text{as-received weight}}{1 + \text{LOI}}
\]

(3)

To determine the Wn content, 1 g of the hydrated sample was dried in an oven at 110 °C for 3 h, and was then ignited at 950 °C in an electric furnace for 1 h. The Wn content of hydrated pastes on the ignited basis was calculated by Eq.(4):

\[
\text{Wn(\%)} = 100 \times \left( \frac{\text{dried weight of paste} - \text{ignited weight of paste}}{\text{ignited weight of paste} - \text{LOI of cement}} \right)
\]

(4)

2.4. Determination \(\text{Ca(OH)}_2\) in hydrated cement pastes

The \(\text{Ca(OH)}_2\) content of hydrated cement pastes was determined by thermal gravimetry analysis (TGA) and calculated based on the ignited weight of the sample.

2.5. Determination of the degree of reaction of calcined coal gangue powder

The determination of the degree of reaction of fly ash was based on a selective dissolution procedure using picric acid-methanol solution and water. The principle of the procedure is that in a blended cement paste, fly ash reacts with calcium hydroxide to form acid-soluble hydration products. It is possible to dissolve the hydration products of cement and fly ash, and the unreacted cement components, leaving the remaining unreacted fly ash undissolved [8].

To determine the degree of reaction of reaction of calcined coal gangue powder, the insoluble residues of the as-received cement and calcined coal gangue powder, and the hydrated AC pastes in a solution of picric acid-methanol-water were determined. One gram of the ground sample was added to a beaker containing 9 g of picric acid and 60 mL methanol (AR Grade). The mixture was stirred using a magnetic stirrer for 15 min. Distilled water (40mL) was added and the mixture was stirred continuously for another 45 min. The mixture was filtered through a Whatman No.41 filter paper. The filter paper and the residue were further washed with methanol until the color of picric acid disappeared. They were then washed with about 300 mL distilled water at about 60 °C. The filter paper and its content were then transferred into a porcelain crucible. The crucible was ignited in an electric furnace at 300 °C, 450 °C and thereafter at 950 °C, each for 1 h. The crucible was weighed after cooling down to room temperature. Blank tests were carried out following the same procedure but without adding the sample. The residue from a blank test was used to correct the weight of residue of the sample.

The residue per gram of ignited sample was calculated by Eq(5):

\[
\text{Residue per gram of ignited sample} = \frac{\text{corrected weight of residue} \times (1 + \text{LOI})}{\text{weight of sample}}
\]

(5)

The unreacted calcined coal gangue powder per gram of ignited AC paste was given by:

\[
\text{Unreacted calcined coal gangue powder per gram of ignited AC paste} = \frac{\text{residue per gram of ignited AC paste} - \text{residue per gram of ignited cement} \times c}{a}
\]

(6)

The degree of reaction of calcined coal gangue powder \(\alpha_a\) was thus given by:

\[
\alpha_a (\%) = 100 \times \frac{(1 - \text{unreacted calcined coal gangue per gram of ignited AC paste})}{\text{residue per gram of calcined coal gangue powder} \times a}
\]

(7)

In Eq.(6) and (7), c and a are original fractions of cement and calcined coal gangue powder, determined according to Eq(2).

3. Results and discussion

3.1. Non-evaporable water of AC pastes with different contents of calcined coal gangue powder

For PC and AC pastes, the results clearly show that the amount of Wn increased as curing age increased. For AC pastes, the amount of Wn is dependent on percentages of cement replacement. Overall, AC pastes had lower Wn contents than the PC paste at the same w/b ratio. The pastes with a lower calcined coal gangue powder replacement had higher Wn contents. Furthermore, it is noted that in the AC pastes, the amount of Wn relative to the cement content (amount of Wn per 100 g of cement) of the paste was higher than in the PC paste, and the higher calcined coal gangue powder contents, the higher relative Wn (Fig. 2). This is consistent with the results of Feldman et al.[9] This is
because when part of cement is replaced by calcined coal gangue powder, the concentration of cement in the system is diluted, and the effective w/c ratio controlling the rate of cement hydration is relatively increased. The results of the determination of Wn content are shown in Table 2.

Table 2. Wn content of PC and AC pastes (based on ignited weight)

| No. | Calcined coal gangue powder replacement (%) | Wn content (%) |
|-----|--------------------------------------------|----------------|
|     |                                            | 3d  | 7d  | 28d  | 60d  |
| AC0 | 0                                          | 9.35| 14.12| 20.34| 22.97|
| AC10| 10                                         | 8.35| 13.56| 20.01| 21.23|
| AC20| 20                                         | 7.68| 12.47| 19.35| 20.64|
| AC30| 30                                         | 7.23| 11.56| 18.29| 19.38|
| AC40| 40                                         | 6.42| 10.87| 16.45| 18.53|

Fig. 2. Wn content relative to the cement content in PC and AC pastes

3.2. Ca(OH)\(_2\) contents

It is generally considered that a fully hydrated PC, with typical C\(_3\)S and C\(_2\)S contents, will take up about 20 to 25 wt.% H\(_2\)O, and produces about 20 to 25 wt.% Ca(OH)\(_2\) [10]. Thus, Ca(OH)\(_2\) content can be used to determine the degree of hydration of cement in the PC pastes. Calcium hydroxide (CH) is known to react with calcined coal gangue powder. However, as the pozzolanic reaction in AC system consumes Ca(OH)\(_2\), the same principle cannot be used to determine the degree of hydration of PC systems.

Table 3. Ca(OH)\(_2\) content of PC and AC pastes (based on ignited weight)

| No. | Ca(OH)\(_2\) content (%) |
|-----|--------------------------|
|     | 3d  | 7d  | 28d  | 60d  |
| AC0 | 12.45| 16.79| 18.37| 19.69|
| AC10| 10.93| 14.73| 13.65| 12.94|
| AC20| 10.12| 13.56| 12.88| 12.36|
| AC30| 9.14 | 12.12| 11.29| 11.16|
| AC40| 7.56 | 9.87 | 9.42 | 9.17 |

Fig. 3. Ca(OH)\(_2\) content relative to the cement content in PC and AC pastes

In this study, Ca(OH)\(_2\) content was determined for part of the samples and the results are shown in Table 3. For PC pastes, the results of Ca(OH)\(_2\) content are consistent with the results of Wn content with an increasing trend with age. As in AC pastes containing calcined coal gangue powder, CH initially increases at early age then drops in the later age (28 days) as it is consumed more and more by pozzolans. The pastes with a lower calcined coal gangue powder replacement had higher Ca(OH)\(_2\) contents. Furthermore, it is noted that for the AC pastes, at the early age (3 days or 7
days) the amount of Ca(OH)$_2$ relative to the cement content (amount of Ca(OH)$_2$ per 100 g of cement) of the paste was similar to that of the PC pastes, but at the later age it is much less than that of the PC paste, and the higher calcined coal gangue powder contents, the lower relative Ca(OH)$_2$ (Fig. 3).

3.3. Degree of reaction of calcined coal gangue powder in AC pastes with different contents of calcined coal gangue powder

Table 4. Degree of calcined coal gangue powder reaction in AC pastes

| No. | Degree of reaction of ignited coal gangue powder (%) |
|-----|-----------------------------------------------|
|     | 3d    | 7d    | 28d   | 60d   |
| AC10| 2.41  | 3.67  | 7.13  | 9.26  |
| AC20| 1.68  | 3.02  | 6.57  | 8.45  |
| AC30| 1.39  | 2.48  | 6.27  | 8.17  |
| AC40| 1.08  | 2.17  | 5.93  | 7.96  |

The results show that at 7 days, a measurable amount of pozzolanic reaction in the AC pastes took place. The reaction degree of about 2% to 3% of the calcined coal gangue powder may correspond to the initial attack on the calcined coal gangue powder particles by the alkali ions in the pore solution [11]. According to Berry et al., even at ages as early as 7 days, calcined coal gangue powder particles are involved in chemical reaction forming ettringite (AFt).

At the age of 60 days, the degree of calcined coal gangue powder reaction increased to about 7% to 9%. The measured degree of calcined coal gangue powder was about three times of that at 7 days. According to Berry et al. [12], during the period of 7 to 60 days, many self-ignited particles show some etching of the amorphous materials, and Ca(OH)$_2$ on calcined coal gangue powder particle undergo redissolution and reaction. At this stage, deposits of reaction products, oriented radially to the calcined coal gangue powder surface, are observable as interfacial or boundary zones around some powder particles. In this stage, various reaction products including hydrates of calcium silicates (CSH), aluminates (CAH), and aluminosilicates (CASH), would be expected to form, with consequent consumption of Ca(OH)$_2$.

Fig. 4 shows the XRD patterns of blended cement with calcined coal gangue powder. The main Ca(OH)$_2$(CH) peaks in blended cement with 10 per cent calcined coal gangue power is the highest among the five cement paste, blended cement with 40 per cent calcined coal gangue power has the lowest peaks of CH. As both Ca(OH)$_2$ and CSH precipitate on the surfaces of calcined coal gangue powder particles, pozzolanic reaction at later ages strengthens the contact between cement and calcined coal gangue powder particles.

From Table 4, it is also noted that calcined coal gangue powder in AC pastes with higher percentages of replacement underwent a lower degree of reaction. This might be due to the lower concentration of Ca$^{2+}$ ions in the pore solutions of the pastes. The effect of calcined coal gangue powder replacement on degree of reaction of calcined coal gangue powder in AC pastes in early age was much than that of in later age. The results show that, in cement pastes with high volumes of calcined coal gangue power, more than 90% of weight of the calcined coal gangue powder remained unreacted after 60 days of curing. This implies that in the high-volume AC systems, the space filling effect is significant.

![Fig. 4. XRD patterns of 28d blended cement with activated coal gangue powder](image)

4. Conclusions

1) Wn contents in AC pastes was lower than that of PC paste at the same w/b ratio. But the amount of Wn relative to the cement content of the AC paste was higher than that in the PC paste, and the higher calcined coal gangue powder content, the higher relative Wn.

2) For the AC pastes, at the early age (3 days or 7 days) the amount of Ca(OH)$_2$ relative to the cement content of the paste was similar to that of the PC pastes, but at the later age, it is much less than that of the PC paste, and the higher
calcined coal gangue powder content, the lower relative Ca(OH)$_2$.

3) Calcined coal gangue powder in AC pastes with higher percentages of replacement underwent a lower degree of reaction. The effect of calcined coal gangue powder replacement on degree of reaction of calcined coal gangue powder in AC pastes in later age was less than that of in early age.

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