The Threshold Value of Effective Replacement Ratio of Fly Ash Mortar Based on Amount of Calcium Hydroxide

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Abstract. The effective mineral admixture in mortar can consume the calcium hydroxide produced by hydration reaction because of pozzolanic effect. For high volume mineral admixture mortar, when the replacement ratio exceeds a certain 'threshold' value, the supply of Ca(OH)² amount is insufficient, the superfluous and ineffective mineral admixture will no longer react in mortar but as fine aggregate. This study presents an experiment study on the threshold value of effective replacement ratio of fly ash mortar by the comprehensive analysis of Ca(OH)² amount and consumption curves. Under the conditions of different curing temperature, the effective replacement ratios of fly ash mortar have been determined ultimately. The results showed that Ca(OH)² amount and consumption in mortar both decreased with replacement ratio. For fly ash mortar, at 20℃ curing temperature, when the replacement ratio was less than 40%, the Ca(OH)² amount decreased obviously with replacement ratio. However, when replacement ratio was more than 40%, Ca(OH)² amount at 91d changed slightly with replacement ratio, the Ca(OH)² amount was consumed to a limit value at this time. Under the condition of 30℃ curing temperature, when the replacement ratio exceeded 30%, the change of Ca(OH)² amount with replacement ratio was close to a straight line, the superfluous fly ash no longer consumed Ca(OH)² basically. Moreover, the consumption of Ca(OH)² was not much difference to the Ca(OH)² amount at the same replacement ratio under the condition of 20℃ curing temperature. This result has a great significance on effective utilization of mineral admixtures in engineering application.

Keywords: Calcium hydroxide, consumption amount, effective replacement ratio, fly ash, mineral material.

1. Introduction
The practical application of high volume mineral admixtures in cement and concrete industry has attracted much attention in recent years. The most worldwide available by-products which can be used as supplementary cementitious materials are fly ash and slag. Fly ash consists of finely divided ashes produced by burning pulverized coal in power stations, and can be categorized as a normal type of pozzolanic to produce high strength and high performance concrete [1]. Nowadays, fly ash has been widely used in production of cement, concrete, cellular concrete, bricks, lightweight construction aggregate and soil stabilization [2]. Many researchers focused on the properties and improvement of concretes containing high-volume fly ash [3]. High-volume fly ash (HVFA) concrete, which has typically 50–60% fly ash as the total cementitious materials’ content, is widely used to achieve the sustainable development of concrete industry [4].
A large fraction of the waste materials consists of blast furnace (BF) slag, which is formed during the making of pig iron by residues from the ore, reducing agents (e.g., coke) and fluxes (e.g., limestone) [5]. Slag can be applied to massive concrete as a mineral admixture, the replacement levels of Portland cement with slag varying from 30% up to 85% are also available, but 50% is usually used in most applications [6]. A significant amount of research has been conducted on concretes containing the high volume slag [7-8]. An economical mix with 80% GGBFS and 20% OPC was nominated for use in the future construction of MC with 154 kg/m³ carbon footprint [9]. A paper presents a comprehensive investigation on the fresh and hardened self-compacting concrete mixtures using slag up to high volume of 90% [10].

Pozzolanic effect refers to the active SiO$_2$ and Al$_2$O$_3$ in mineral admixture, which can react with the alkaline activator Ca(OH)$_2$ produced by hydration reaction, and additional calcium silicate hydrate (C-S-H) gel are formed to densify the matrix that leads to higher strength and better durability [11]. With the increase of the replacement ratio of mineral admixture in mortar or concrete, the cement content reduced and the Ca(OH)$_2$ amount produced by hydration decreased; when the replacement ratio exceeds a certain 'threshold' value, Ca(OH)$_2$ amount in mortar will be almost consumed completely and not enough, the superfluous mineral admixture in mortar would no longer react with Ca(OH)$_2$ to form C-S-H gel as cementing material but be filled in the mix like sand.

In this study, because the curing conditions had a significant effect on the properties in the hardened state of mineral admixture mortars [12], and active mineral admixture material is comparatively sensitive to the curing condition, the mortars were placed under the condition of different curing temperatures. By the differential thermal analysis (DTA/TG) method, the Ca(OH)$_2$ amount and consumption of Ca(OH)$_2$ in mortar were obtained. Through the comprehensive comparison and analysis, the effective replacement ratios of different mineral admixtures in mortar were determined ultimately under the condition of different curing temperatures.

### 2. Experimental

#### 2.1. Materials and Mix Proportions

According to Japanese Industrial Standard (JIS) R5210, an ordinary Portland cement was used in this study. Two kinds of mineral admixtures, ordinary II-level fly ash conforming to (JIS) A6201. The detailed chemical compositions of these materials are shown in table 1.

The mix proportions of fly ash mortars are provided in table 2. Regarding the mix proportion of mortar, the volume ratio of paste and sand in mortar was determined as 1:1 in order to emphasize the changes of paste in mortar. The water to binder ratio (W/B) of 0.5 is used to prepare paste and mortar specimens throughout the experimental program, the replacement ratios of fly ash in mortar are designed as 0, 10, 20, 30, 40 and 50%, respectively.

#### 2.2. Experiment Method

The mortar specimens with Φ50×100mm cylinders were prepared for test. In order to study the curing temperature’s influence on the effective replacement ratio of mineral admixture in mortar, one group of specimens after mould-releasing were placed in a water bath at 23±2 °C while the other group of specimens were placed in a water bath at 30 ± 2 °C curing temperature until the age of testing. The curing ages were set as 28 and 91 days.

| Type      | Ig.loss(%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO   | SO$_3$ | Na$_2$O | K$_2$O | TiO$_2$ |
|-----------|------------|---------|-------------|-------------|------|-------|--------|--------|-------|--------|
| Cement    | 0.7        | 19.54   | 4.68        | 3.17        | 65.66| 1.77  | 2.99   | 0.28   | 0.57  | 0.28   |
| Fly ash   | 0.9        | 57.36   | 28.68       | 4.29        | 2.41 | 1.28  | 0.35   | 0.73   | 0.83  | 1.92   |
Table 2. Mix proportion of Fly ash mortar.

| NO. | W/ (F+C) (%) | Replacement ratio (%) | Unit dosage(kg/m³) |
|-----|--------------|-----------------------|-------------------|
|     |              |                       | W    | C    | FA   | S    |
| Fly Ash | 50        |                       | 306  | 612  | 0    | 1310 |
|        | 10         |                       | 300  | 540  | 60   | 1310 |
|        | 20         |                       | 295  | 472  | 118  | 1310 |
|        | 30         |                       | 294  | 412  | 176  | 1310 |
|        | 40         |                       | 288  | 345  | 230  | 1310 |
|        | 50         |                       | 282  | 282  | 282  | 1310 |

Differential thermal analysis was used to measure the residual and consumption amount of Ca(OH)$_2$ in different mineral admixture mortars by an analytical device (maximum temperature is 1500°C). The hardened part of mortar at which the hydration reaction has stopped was cut into small pieces by a long flat nose pliers with side cutting, ground into powder by contusion mortar, the powder through 40μm sieve has been collected as the samples for test.

The residual amount of Ca(OH)$_2$ in mortar was generated approximately at 460 °C-510 °C by dehydration reaction, and the decrement of the dehydration region can be read from the peak of DTA value. In addition, more than 600 °C, a part of calcium carbonate would conduct a decarbonation reaction, therefore the decrement at 600 °C is regarded as the amount of bound water. The amount of calcium hydroxide are expressed as the weight per unit weight of mineral admixture in this study. The amounts of calcium hydroxide in different mineral admixture mortars have been tested at the age of 28 and 91 days.

3. Results and Discussion

3.1. Ca(OH)$_2$ Amount in Fly Ash Mortar

Figure 1 showed the changes of Ca(OH)$_2$ amount during the curing period under the condition of 20 °C curing temperature. When replacement ratio is 0%, the CH amount in cement mortar increased with curing age because of hydration reaction of cement. However, when the replacement ratio is less than 40%, the CH amount of fly ash mortar was increased at first and decreased subsequently with curing age. The main reason is that replacement ratio of fly ash in mortar is relatively lower, the pozzolanic effect of fly ash at early age was not activated fully under the condition of 20 °C curing temperature, the CH amount consumed by fly ash was far less than the amount produced by cement; At the long-term age, a large amount of CH was consumed because of fully activated pozzolanic effect. In addition, it can be seen that the Ca(OH)$_2$ amount at 50% replacement ratio decreased with the age.

Figure 2 showed the changes of Ca(OH)$_2$ amount during the curing period at 30°C curing temperature. Similarly, the CH amount in normal cement mortar also increased with curing age. On the contrary, the CH amount of fly ash mortar decreased with curing age. The main cause is that higher temperature accelerated the hydration reaction of cement and more fully activated the pozzolanic effect of fly ash at the early age, a large amount of CH has been consumed by fly ash in mortar.

Figure 3 illustrated the relationship between Ca(OH)$_2$ amount and replacement ratio under the condition of 20 °C curing temperature. Because the pozzolanic effect of fly ash in mortar was slightly activated at 28d, CH amount mainly came from the hydration reaction of cement in mortar, CH amount of fly ash mortar at 28d decreased obviously as replacement ratio increased. In comparison with the curve at 28d, there were two obvious turning points for the CH amount curve at 91d, at 10% and 40% replacement ratio, respectively. On the first turning point, compared with normal cement
mortar, the CH amount was consumed by fly ash in mortar at 10% replacement ratio, resulting in a sharp fall of CH amount. However, on the second turning point, when the replacement ratio is lower than 40%, the CH amount produced by the hydration reaction of cement was sufficient, and can be fully reacted with the fly ash in mortar to form the C-S-H gel, so the CH amount decreased obviously and is a linear relationship with replacement ratio. However, more than 40%, the effective fly ash in mortar almost completely reacted with CH but there is still a small amount of CH remains in the mortar, the superfluous fly ash would no longer consume the CH but be filled in mortar as fine aggregate, the decrement of CH amount was slight and slow with replacement ratio.

Figure 1. CH amount of fly ash mortar at 20℃.

Figure 2. CH amount of fly ash mortar at 30℃.

Figure 3. CH amount with replacement ratio at 20℃.

Figure 4. CH amount with replacement ratio at 30℃.

Figure 4 illustrated the relationship between Ca(OH)₂ amount and replacement ratio under the condition of 30 ℃ curing temperature. The CH amount of fly ash mortar at 28d and 91d both decreased obviously as replacement ratio increased. It can be seen that there also were two obvious turning points for the CH amount curve at 91d. On the first turning point, at 10% replacement ratio, it is the same as the point under the condition of 20 ℃ temperature. Unlike the condition of 20 ℃ temperature, the second turning point of CH amount curve appeared at replacement ratio of 30%, the turning point moved forward. This showed that higher curing temperature also had a great influence on the turning point of CH amount curve. More than 30%, CH amount produced by hydration reaction of cement was insufficient, CH was reacted to a lower value and the superfluous fly ash no longer consumed CH, the variation of CH amount with replacement ratio was very slight, close to a straight line.
3.2. Consumption of CH in Fly ash Mortar
The above has discussed the changes of CH amount in fly ash mortar with curing age and replacement ratio, in this part, the CH amount consumed by unit fly ash amount in mortar was studied and calculated. According to equation (1), the consumption of CH amount by 1g fly ash could be calculated.

$$CH_A = \frac{(CH_{PC} \times (1-r) - CH_{FA})}{r}$$

(1)

Where:
- $CH_A$ = Consumption of CH amount by 1g fly ash [g]
- $CH_{PC}$ = CH amount in normal cement mortar [g]
- $CH_{FA}$ = CH amount in fly ash mortar at the replacement ratio of r [g]
- $r$ = Replacement ratio

Figure 5. Relationship between consumption of CH and replacement ratio.

Figure 5 illustrated the relationship between the consumption of CH and replacement ratio at 20 and 30 °C curing temperature. The consumption of CH decreased with replacement ratio of fly ash in the mass, the smaller the replacement ratio, the supply of CH amount in mortar was more sufficient, the consumption of CH by fly ash per unit in mortar was higher. In addition, because the higher temperature can accelerate the hydration reaction and pozzolanic reactivity of fly ash in mortar, the consumption of CH in mortar at 30 °C curing temperature was higher than that at 20 °C.

The pozzolanic effect of fly ash in mortar was slightly activated at 28 days, the consumption of CH amount slightly decreased with replacement ratio, the consumption of CH amount at 30 °C was slightly higher than that at 20 °C; at the long-term age, the consumption of CH at 30 °C was far higher than that at 20 °C at the replacement ratio of 10%, the main cause is likely that there placement ratio was relatively lower, the supply amount of CH was sufficient, much more CH amount was consumed at 30 °C because of more fully activated pozzolanic effect. However, when replacement ratio exceeded 30%, at the replacement ratio of 40% and 50%, the consumptions of CH at 91d under the condition of different curing temperatures were almost same. This is likely because the supply amount of CH is not sufficient, the CH amount in mortar has been almost completely consumed to a low limit, and the increase of curing temperature has no effect on the consumption of CH amount at the long term age.

From what has been discussed above about the CH amount, we may safely draw the conclusion that the maximum effective replacement ratio of fly ash in mortar should be considered as 40% under the condition of 20 °C curing temperature; while 30% under the condition of 30 °C curing temperature.
4. Conclusions

The following results were obtained from this study:

1) From the turning point of \( \text{Ca(OH)}_2 \) amount curve, it can be seen that the threshold value of effective replacement ratio of fly ash mortar at 20 °C curing temperature should be considered as 40%.

2) The curing temperature has an influence on the maximum effective replacement ratio. The threshold value of effective replacement ratio of fly ash mortar at 30 °C curing temperature should be considered as 30%.

3) When replacement ratio exceeded 30%, at the replacement ratio of 40% and 50%, the consumptions of \( \text{Ca(OH)}_2 \) at 91d under the condition of different curing temperatures were almost same.

4) Based on this study, the effective utilization of fly ash could be realized in the practical engineering application without a significant loss in properties of concrete.

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References

[1] Phuong Trinh Bui, Yuko Ogawa, Kenichiro Nakarai, Kenji Kawai, “A study on pozzolanic reaction of fly ash cement paste activated by an injection of alkali solution”, Constr and Build Mater, Volume 94, 30 September 2015, pp. 28-34.

[2] Tayfun Çiçek, Yasin Çınçin, “Use of fly ash in production of light-weight building bricks”, Constr and Build Mater, Volume 94, 30 September 2015, pp. 521-527.

[3] Fernando S. Fonseca, Robert C. Godfreyb, Kurt Siggardc, “Compressive strength of masonry grout containing high amounts of class F fly ash and ground granulated blast furnace slag”, Constr and Build Mater, Volume 94, 30 September 2015, pp. 719-727.

[4] Xiao-Yong Wang, Ki-Bong Park, “Analysis of compressive strength development of concrete containing high volume fly ash”, Constr and Build Mater Volume 98, 15 November 2015, pp.810–819.

[5] Maja A. Larsson, Stijn Baken, Erik Smolders, Francesco C, “Vanadium bioavailability in soils amended with blast furnace slag”, Journal of Hazardous Materials 296(2015), pp. 158-165.

[6] C.H. Huang, S.K. Lin, C.S. Chang, “Mix proportions and mechanical properties of concrete containing very high-volume of Class F fly ash”, Constr. Build. Mater. 46 (2013), pp. 71-78.

[7] Anderson, K.W, Uhlmeyer, J.S. Williams, K., Russell, M, “Evaluation of Portland cement concrete pavement with high slag content cement”, Final Report WA-RD 728.2, Washington State Department of Transportation, October 2013.

[8] V. Sivasundaram, V.M. Malhotra, “Properties of concrete incorporating low quantity of cement and high volumes of ground granulated slag”, ACI Mater. J., 89 (6) (1992), pp. 554-563.

[9] M. Elchalakani, T. Aly, E. Abu-Aisheh, “Sustainable concrete with high volume GGBFS to build Masdar City in the UAE”, Case Stud. Constr. Mater., 1 (2014), pp. 10–24.

[10] Kali Prasanna Sethy, Dinakar Pasla, Umesh Chandra Sahoo, “Utilization of high volume of industrial slag in self compacting concrete”, Journal of Cleaner Production, 28 August 2015.

[11] Vagelis G, Papadakis, “Effect of fly ash on Portland cement systems Part II. High-calcium fly ash”, Cem Concr Res, 30 (2000), pp.1647-1654.

[12] Axel Schölera, Barbara L, “Hydration of quaternary Portland cement blends containing blast-furnace slag, siliceous fly ash and limestone powder”, Cement and Concrete Composites ,55(2015), pp.374-382.