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# Evaluation of calcium hydroxide contents in pozzolanic cement pastes by a chemical extraction method

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ABSTRACT

The aim of the study is to investigate the calcium hydroxide ($Ca(OH)_2$) contents in pozzolanic cement pastes analyzed by the chemical extraction method and thermal analysis (DTA/TG). The second part of the study involves the carbonation of pozzolanic cement pastes and its influence on $Ca(OH)_2$ reduction. The $Ca(OH)_2$ contents in cement pastes after being subjected to accelerated carbonation were investigated by a chemical extraction method and compared to those values from DTA/TG analysis. The experimental results show that the chemical method reveals overall results comparable to those from DTA/TG analysis. However, in case of pastes containing high amounts of mineral admixtures or pastes subjected to carbonation which contain very low $Ca(OH)_2$, only the chemical method yields precise reliable results by showing the pseudo-negative contents.

## 1. Introduction

The calcium hydroxide ($Ca(OH)_2$; referred to as CH from this point on) content is regarded as a major parameter concerning passivity condition of concrete. The high pH of concrete pore solution provides thin protective film layer covering the reinforcing bars and protecting them from corrosion and rusting. The amount of CH in cement paste, mortar and concrete can be determined by several methods. Nevertheless, different methods yield different results. Moreover, for the modern concrete where cement has been replaced by a plenty amount of mineral admixtures, the total CH content in those mixes are much lower compared with the original Portland cement mix. On the other hand, when concrete has been subjected to the environment, the CH is also slowly reduced by the consumption of carbonation attack. These influences lead to more difficulty in the analysis, especially in the studies on depassivation of concrete and their effect on the steel reinforcement corrosion. The application of the widely used method, DTA/TG, on these kinds of mixtures is still doubtful [1]. Various studies [2–4] proposed several solvents to dissolve CH from cement paste powder, which can be determined by titrating the resulting solution with a suitable acid. However, the techniques are questionable as they also appear to attack other hydration products which then overestimate the results of CH content [1,5]. For instance, it has been reported that the analysis results from the method proposed by Franke [2] yielded the CH contents higher than those from DTA/TG for about 2–7% [1]. Although the utilization of the chemical pH indicator such as phenolphthalein is also applicable to evaluate the passivity condition, however, it yields only the qualitative results. The method can differentiate between fully carbonated and non-carbonated area which might vary between being completely unaltered and being slightly carbonated. The limitation of the techniques is a major obstacle in the study of high volume pozzolanic replacement concrete.

From previous study [1], the new chemical method for determining CH has been proposed. The benefit of the method is mainly expected on testing of very low CH content cement paste and mortar or concrete mixtures, which exceeds the capability of DTA/TG analysis. The principal of the chemical method bases on the instability of CH phase in appropriated pH solvent, where CH is dissolved without other hydrated phases deterioration.

To observe the limit of the chemical method, the cement pastes containing very high amount of mineral admixtures were investigated in this study. On the other hand, it is generally known that carbonation attack also consumes the CH contained in cement paste matrix. The process reduces the alkalinity of concrete which causes the embedded reinforcement bar be depassivated and corroded in long-term. Therefore, the residual CH in cement paste after carbonation is also an important information, and was in this study.

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## 2. Experimental investigation

The experiment includes cement paste samples of ordinary Portland cement (CEM I 42,5 R) and blast-furnace slag cement (CEM III/B 42,5 N), with up to 50% by weight of Class-F fly ash replacement. The mix proportions are shown in Table 1. The chemical compositions of cements and fly ash used in this study are given in Table 2. To prepare cement pastes used in the analysis, the binders were weighted and proportional mixed in a commercial Hobart mixer for 1 min. Then, the pre-weighted amount of deionized water was added, and mixed with the powder for 5 min. The fresh paste mixture was poured into the prism moulds (40 × 40 × 160 mm) and vibrated on a vibrating table to remove entrapped air. Finally, the moulds were covered with glass plates, and then stored in a curing box held at 100% RH environment. After 24 h, the moulds were removed, and all samples were cured under damp sacking in a 100% relative humidity curing box until the age of testing.

The tests were conducted at the age of 7, 14, 28, 90, 180 and 365 days. When samples reached the age to be tested, the prism bars were taken from the curing box. One-centimeter thick specimens were cut by a machine saw, and the balances were returned to the curing box. The cut specimens were dried in an oven at 105 °C for 3 days to ensure that most water has been evaporated, and then finely ground in a planetary ball mill. After that, the powders were dried at 105 °C for 1 day to remove all residual moisture. Finally, the powders were kept in a closed glass chamber containing silica gel and natronasbest, which provides a humidity and $CO_2$ free environment.

To evaluate the CH contents in carbonated cement pastes, the *w/b 0.35* specimens which have the age of 180-day were thin-sliced to have a thickness of about 2–3 mm. The tests were conducted at the carbonation period of 6 h and 1, 2, 5 and 9 days. The sliced specimens were subjected to the accelerated carbonation by storing in the carbonation chamber which held a 3% carbon dioxide concentration and 65% of relative humidity, constantly. Eventually, the carbonated samples were oven-dried and ground to fine powder.

Apart from DTA/TG, the CH in cement pastes was analyzed by the chemical extraction method. As proposed in previous study [1], the finely ground paste powder was dissolved into the water-based solvent made of 1 g/l CH solution. The solution with powder was shaken for 24 h, and then titrated with 0.1 M $HNO_3$. The amount of acid required was determined and compared to the control solution. The amount of CH dissolved from the powder can be calculated from the different acid requirements in titrations. The chemically bound water has to be investigated to calculate the factor of further reaction. The detail of the method was explained in the previous studies [1,6]. However, to have a standard control powder for present and future experiments, the ground quartz sand powder was used as a control substance in this study. In addition, all samples analyzed in present work were done by the method, which the suspended powder was removed before titration. It does not matter how much the CH content in the specimen. It would be remarked that the result of CH content was obtained from the average of two measurements.

**Table 1**
Mix proportions of cement paste mixtures in weight ratio.

| Mix no. | Mixtures binder type – *w/b* ratio | CEM I 42,5 R | CEM III/B 42,5 N | Fly ash | Water |
|---|---|---|---|---|---|
| 1.1 | CEM I 0.35 | 100 | – | – | 35 |
| 1.2 | CEM I 0.50 | 100 | – | – | 50 |
| 1.3 | CEM I 0.60 | 100 | – | – | 60 |
| 2.1 | CEM I + 25FA 0.35 | 75 | – | 25 | 35 |
| 2.2 | CEM I + 25FA 0.50 | 75 | – | 25 | 50 |
| 2.3 | CEM I + 25FA 0.60 | 75 | – | 25 | 60 |
| 3.1 | CEM I + 50FA 0.35 | 50 | – | 50 | 35 |
| 3.2 | CEM I + 50FA 0.50 | 50 | – | 50 | 50 |
| 3.3 | CEM I + 50FA 0.60 | 50 | – | 50 | 60 |
| 4.1 | CEM III 0.35 | – | 100 | – | 35 |
| 4.2 | CEM III 0.50 | – | 100 | – | 50 |
| 4.3 | CEM III 0.60 | – | 100 | – | 60 |
| 5.1 | CEM III + 50FA 0.35 | – | 50 | 50 | 35 |
| 5.2 | CEM III + 50FA 0.50 | – | 50 | 50 | 50 |
| 5.3 | CEM III + 50FA 0.60 | – | 50 | 50 | 60 |

**Table 2**
Chemical composition of cements and fly ash used in the experiment.

| Oxide content (%wt.) | CEM I 42,5 R | CEM III/B 42,5 N | Fly ash |
|---|---|---|---|
| $SiO_2$ | 20.9 | 30.1 | 50.5 |
| $Al_2O_3$ | 5.5 | 10.1 | 24.7 |
| $Fe_2O_3$ | 2.8 | 1.0 | 7.2 |
| CaO | 63.9 | 48.2 | 5.5 |
| MgO | 1.5 | 6.8 | 2.0 |
| $SO_3$ | 3.3 | 2.5 | *n.i.*[a] |
| $K_2O$ | 0.9 | 0.3 | 4.1 |
| $Na_2O$ | 0.2 | 0.3 | 0.8 |

[a] *n.i.: not investigated.*

## 3. Results and discussion

### 3.1. Influences of mineral admixtures and water to binder ratio on calcium hydroxide content in cement pastes

Fig. 1a–c demonstrates the results of CH contents in cement paste samples analyzed by the chemical extraction method. The results of analysis were compared to those from DTA/TG as shown in Fig. 2. In general, the CH contents determined by the chemical method are approximately 1–3% lower than those from DTA/TG.

As seen in Fig. 1a–c, the initial CH contents in CEM I mixes were produced rapidly at early ages. It is generally known that CH is one of the main products of calcium silicates ($C_3S$ and $C_2S$) hydrations which react more rapidly than other phases. The CH ascends over 80% of the ultimate content within 3 days. Thereafter, the rate of CH production becomes slower. The CH contents continue to rise for a period until the maximum value is reached, then start to drop. The similar phenomenon was also found in the literature [7], where the cement paste samples were analyzed by DTA/TG method. There is no clearly explanation on the phenomenon, but it may be due to the loss of CH to the damp cloth which was used as a curing medium. If the rate of CH produced from the hydration of cement is lower than the rate of CH diffused to the curing medium, the amount of CH in the sample may slightly reduce.

Typically, the initial CH contents depend mainly on the fraction of cement content in the matrix. Therefore, it is clearly seen that all mixtures which contain higher amounts of slag or fly ash show the less initial CH contents (at 3–7 days). After that, the CH contents were further decreased by the consumption of the pozzolanic reaction. The CH contents decrease as slag and fly ash replacement increases.

The results showed that *w/b* ratio also influences the production of CH in cement pastes. The maximum CH developed in the mixtures seem to have a relationship to *w/b* ratio. For mixture with higher *w/b* ratio, there is more free water for reactions and better dispersion of the powders. Hence, the increasing of *w/b* ratio causes the higher CH production in pure CEM I mixtures due to the better hydration of cement, but lowering the amount of CH in pozzolanic mixtures owing to the higher reactivity of pozzolanic reaction. In long-term, the more free water also readily motivates the pozzolanic reaction of fly ash. It can be obviously seen that,