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A new chemical method for analyzing free calcium hydroxide content in cementing material

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Abstract

Using pozzolanic components in concrete mixtures has several considerable benefits. However, the description of understanding on many of the properties of such concretes and structures is still doubtful, especially concerning the steel corrosion protection capacity. As generally known, the amount of calcium hydroxide [$Ca(OH)_2$] contained in a concrete sample plays an important role for steel passivity and corrosion resistance, especially the buffering capacity subjected to depassivating phenomena. When cement in a concrete mixture is replaced by pozzolan, the total lime content in the concrete decreases, which may lead to a faster and higher carbonation and corrosion rate of the embedded steel reinforcement. The study proposes a new appropriate testing method for investigating small amounts of hydroxide content in cement paste, mortar applied, or concrete, especially for pozzolanic cementing materials. The new chemical procedure is conducted on several samples, and the results are compared with those of other well-known methods, namely, DTA and Franke method. The results show that the new method gives results comparable to the result from DTA analysis. In case of very low $Ca(OH)_2$ content analysis of artificial sample containing pozzolanic additions, only the proposed new analyzing method yields precise reliable results.

Keywords: Analyzing method; $Ca(OH)_2$; Corrosion; Fly ash; Granulated blast furnace slag

1. Introduction

Recently, pulverized fly ash and granulated blast furnace slag are the industrial by-products, which are well known and widely used as a part of concrete material. Fly ash is the by-product mineral residue produced by burning coal, collected from the power plant's exhaust gas by electrostatic precipitator, while slag is the by-product from the iron manufacture. From both environmental and economical points of view, fly ash and slag are very attractive to use in concrete material, as in concrete mixture or interground with Portland cement clinker.

The concrete mixtures containing fly ash or blast furnace slag are commonly used in construction works for many purposes, especially as a low-heat concrete for massive structures or as a high-performance concrete. Good quality pozzolana can improve many concrete properties, such as increasing workability, reducing heat generation, improving some durability aspects, and many more.

However, as generally known, the calcium hydroxide [$Ca(OH)_2$] produced from hydration of Portland cement is partially consumed by the pozzolanic reaction of blast furnace slag and fly ash. The steel rebars in reinforced concrete are preserved from the corrosion by a thin passive oxide film formed on their surface due to the high-alkaline environment of the surrounding concrete. In a long-term basis, lack of $Ca(OH)_2$ in pozzolanic concrete can cause depassivation that induces corrosion problems to the steel reinforcement.

The problem is relevant in the context of increasing the use of composite cements with high amounts of pozzolanic fillers. To find out the limits of acceptable filler amounts, it is necessary to have a reliable method to determine small amounts of $Ca(OH)_2$ content in concretes. Therefore, the aim of the study is to propose a new appropriate testing method for investigating small amounts of hydroxide content in cement paste, mortar, or concrete, especially for pozzolanic cementing materials.

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2. Experimental work

Thermogravimetry (TG) is one of the worldwide methods used most for measuring various phases contained in hardened cementing material. In the temperature range of 450–500 °C, weight loss determined using DTA was loss of water from $Ca(OH)_2$, the result of which can be interpreted to be the free $Ca(OH)_2$ content in weight percentage by the computational method of Marsh [1]. Therefore, this DTA method was chosen to measure the free $Ca(OH)_2$ content in the sample, and the results were compared to the titration method proposed here.

On the other hand, there are various chemical methods that have been proposed for extracting free lime in calcium silicate hydrate (C–S–H) phases [2–4]. In the past, various solvents were also proposed by many researchers for dissolving free $Ca(OH)_2$ in cement paste, which can be later determined by titrating the resulting solution with a suitable acid. However, the most well known procedure that uses acetoacetic ester and isobutyl alcohol to dissolve free CaO or $Ca(OH)_2$ is called Franke method [2].

To dissolve the free lime according to Franke method, 0.05–1.0 g of cement paste powder is placed in a 200-ml flask. Add 3 ml of acetoacetic ester and 20 ml of isobutyl alcohol. Then, reflux the solution for 1 h on a hot plate. Cool the mixture and filter it with suction pump using dense filter paper. Finally, wash the flask, residue, and filter paper with 20 ml of isobutyl alcohol. The $Ca(OH)_2$ that was initially in sample powder is now dissolved in the filtrated solution, and it can be determined by titration with 0.1 M hydrochloric acid, using bromophenol blue as the chemical indicator.

In the present study, a new $Ca(OH)_2$ extraction method is proposed. The concept of $Ca(OH)_2$ analysis by this new investigating method takes into account the stability of cement hydration phases under various pH conditions. As generally known, all hydrated cement phases are stable in specific defined ranges of alkalinity environment. The phases are subjected to decompose when pH of the test solution is lower than the stability levels. Portlandite [$Ca(OH)_2$] is at first destabilized, and at lower pH values, the C–S–H, C–A–H, and the others are dissolved. Table 1 shows the stability of $Ca(OH)_2$ and C–S–H phases under various pH values. The target of the testing is to extract $Ca(OH)_2$ from the cement paste into the solvent without deteriorating other hydrated phases.

Several sources of samples were used in the study. The experimental work is including the samples of pure OPC type CEM I cement paste, slag cement paste, and fly ash blended cement paste. The samples with a range of 0.35 to 0.65 water–cement ratio, 0% to 60% fly ash replacement, and 28 days to 3 years of age were used in the investigation.

To extract portlandite from the sample, a certain amount of ground sample was diluted in 200 ml of filtrated $Ca(OH)_2$ solution (concentration: 1 g substance/1 l $Ca(OH)_2$ solution) in a plastic bottle, which was called sample solution. As a control solution with a dummy sample to neutralize the effect of suspended solid on pH measurement or filtration comparing with sample solution, a $Ca(OH)_2$-free concrete powder was mixed with the $Ca(OH)_2$ solution with the same amount of the sample powder weight in the sample solution. This hydroxide-free concrete powder used as control sample was made from slag cement with high fly ash replacement concrete. Before using, this hardened slag cement–fly ash concrete was ground and put into the glass chamber with a high-carbon-dioxide concentration to make sure that no residual $Ca(OH)_2$ remained. Both sets of solution bottles were shaken by the rotating table for 1 day. The amount of sample should not be too much or too less to ensure the precision of the test. The recommended weights of the samples used in testing according to their hydroxide content are demonstrated in Table 2.

Table 1
Solution compositions for the isothermally invariant points in $CaO–SiO_2–H_2O$ system at 25 °C [5]

Solids in equilibrium	Ca (m mol/kg)	Si (m mol/kg)	pH
SH am.	0	1.41	6.38
SH am.+C–S–H (0.8)	1.52	4.18	10.17
C–S–H (0.8)	1.23	1.55	10.88
C–S–H (0.8)+C–S–H (1.1)	1.25	1.47	10.91
C–S–H (1.1)	1.23	1.12	11.03
C–S–H (1.1)+C–S–H (1.8)	19.3	2.45×10^{-2}	12.43
$Ca(OH)_2$+C–S–H (1.8)	22.0	1.90×10^{-2}	12.53
$Ca(OH)_2$	21.9	0	12.52

SH am. – amorphous silica gel.

The decomposition rate of hydrated cement phases in solution mainly depends on the nature of their hydration products, especially C–S–H species. The chemical compositions of these phases depend on the initial oxide composition, water–cement ratio, curing temperature, and age. The C–S–H can be classified according to the $CaO–SiO_2$ ratio. C–S–H with high $CaO–SiO_2$ ratio and $Ca(OH)_2$ are the major compounds in hardened OPC paste, while C–S–H with the low $CaO–SiO_2$ ratio is the main hydration product in pozzolan cement paste. For pure cement paste containing no pozzolan, the very high pH is needed to obtain the $CaO–SiO_2$ ratio close to the initial $CaO–SiO_2$ values and to sustain its stability.

Therefore, the determination of $Ca(OH)_2$ in cementing material by titration method is classified into two methods according to the range of $Ca(OH)_2$ content in the sample. For the very low $Ca(OH)_2$ sample analysis, the $Ca(OH)_2$ content less than 1 wt.%, both sample solution and control solution were titrated with 0.1 M HNO_3 directly after the mixing period to determine the amount of different hydroxide contained, down to the endpoint of pH 12.0, measured by pH meter during continuous moving by magnetic stirrer. The $Ca(OH)_2$ amount of the sample is corresponding to the difference of acid needed for reaching the endpoint of the sample solution and of the control solution.

Table 2
The recommended sample weights for analysis

$Ca(OH)_2$ content in sample (%)	Weight of sample (g)
0–5	1–2
5–10	0.50
>10	0.25

In case of high-$Ca(OH)_2$-content samples, because of their instability under the pH lower than about 12.50, the solid residue has to be removed before titration testing. After mixing for a day, both the control and the solution samples were filtrated with a dense filter paper. The bottle, sample residue, and filter paper were washed with 50 ml of ethanol. Finally, the $Ca(OH)_2$ contained in the sample is now in the filtrated solution and can be determined by titration test, as shown in the previous case. However, because all solids have been removed, the end point of titration can be set at a pH close to the neutral point (pH 7); the use of chemical indicator is also possible.

From the titration results, the percentage of $Ca(OH)_2$ content in the sample was determined using the following relation:

$$\text{mol OH}^- \ [\text{from Ca(OH)}_2]$$
$$= \text{mol H}^+ \ (\text{from 0.1 M HNO}_3)$$

$$2\frac{\frac{\text{CH}\%W_\text{s}}{100}}{M_\text{CH}} = \frac{0.1\ V}{1000}$$

finally,

$$\text{CH}\% = \frac{0.37\ V}{W_\text{s}} \tag{1}$$

where M_{CH} is a molecular weight of $Ca(OH)_2$ which is equal to 74, CH% is the $Ca(OH)_2$ content (wt.%), V is volume of the acid difference (ml), and W_S is weight (g) of sample used in the analysis.

However, the result from the above equation is only the preliminary result. When the sample was dissolved in the $Ca(OH)_2$ solvent, which is the water-based solution, the further hydration would occur during shaking, and this result would affect the total $Ca(OH)_2$ amount dissolved into the solvent.

During the dissolving of the powder in the water-based solution, a possible hydration of cement continues in the solution, and additional $Ca(OH)_2$ is produced from this second-state reaction. This undesired part of extra $Ca(OH)_2$ should be determined and subtracted from the total content to finally obtain the real $Ca(OH)_2$ amount contained in the sample originally. In case of fly ash, because the solvent has a pH value of about 12.5, this too low alkalinity environment cannot breakdown the glass structure of the fly ash, which requires a pH of about 13.2 or 13.3 to decompose [6,7], so that the advance pozzolanic reaction of fly ash in the solution would not occur or can be neglected.

The correcting factor of the extra reaction is proposed to be based on the degree of hydration. To determine the hydration degree factor, about 2–3 g of the original sample powder is mixed with a few amount of deionized water in a small bottle for 1 day to simulate the further hydration occurring during the dissolving process. After that, the sample sludge is dried under 105 °C for 1 day. Then, it is ready for the according chemical bound water content testing.

Both the prepared samples, initial and posthydrated, are burned in the high-temperature furnace, which keeps the temperature constant at 1000 °C, lasting for 30 min. After the process, the amount of chemical-bound water in the samples equal to the weight loss is measured by weight.

Then, the hydration degree factor used as a correcting factor for adjusting the $Ca(OH)_2$ content result in Eq. (1) is used as shown below:

$$\text{CH}\%^* = \frac{W_\text{CBW,i}}{W_\text{CBW,f}}(\text{CH}\%) \tag{2}$$

where CH%* is the adjusted $Ca(OH)_2$ content, CH% is the $Ca(OH)_2$ content obtained from Eq. (1), and $W_{CBW,i}$ and $W_{CBW,f}$ are the chemical bound water (wt.%) before and after posthydration, respectively.

3. Results and discussion

3.1. Results for higher $Ca(OH)_2$ content paste samples

Test results in $Ca(OH)_2$ content in high-content fly ash cement paste samples tested by direct titration (no filtering) are given in Table 3. The result shows that the more the cement paste contains fly ash, the less $Ca(OH)_2$ content is present. In addition, $Ca(OH)_2$ content in paste also depends on the water–binder ratio and age of the sample. The table also compares the results between analyses by the new chemical method testing and DTA testing. Inasmuch as they showed a good relation, the results of $Ca(OH)_2$ content tested by the new method, including hydration correction factors, are comparable to those of DTA testing.

To determine the limits of the testing methods, testing on the extremely high pozzolanic content cement pastes has been performed. To achieve this task, a high-slag-content cement, according to the German standard (DIN 1164-1: CEM III B), was used. The results from the analysis by the new chemical method, in comparison to DTA on the cement paste made from slag cement blended with 50 wt.% fly ash, which gave an absolutely low amount in $Ca(OH)_2$ content, are shown in Fig. 1.

DTA was not able to detect any hydroxide because of the too low contents beyond the limit of DTA testing possibility. DTA show the 0% content for all samples in this series, but the new chemical method could detect the contents precisely.

Table 3
Comparison results of $Ca(OH)_2$ content in cement paste analyzed by the new chemical method and DTA method

Sample no.	Sample description	$Ca(OH)_2$ from DTA (%)	$Ca(OH)_2$ from the new chemical method (%)
P1	Type I cement+50% FA; W/B 0.35; 28 days	4.30	5.80
P2	Type I cement+50% FA; W/B 0.35; 3 months	3.80	3.50
P3	Type I cement+50% FA; W/B 0.35; 22 months	1.50	–
P4	Type I cement+50% FA; W/B 0.50; 28 days	3.60	3.37
P5	Type I cement+50% FA; W/B 0.50; 3 months	2.60	2.60
P6	Type I cement+50% FA; W/B 0.50; 22 months	1.10	1.20
P7	Type I cement+50% FA; W/B 0.65; 28 days	4.30	–
P8	Type I cement+50% FA; W/B 0.65; 3 months	2.50	2.30
P9	Type I cement+50% FA; W/B 0.65; 22 months	0.80	0.88
P10	Type I cement+50% FA; W/B 0.50; 3 years	1.10	1.14

This performance of the new chemical testing method for very low $Ca(OH)_2$ contents fulfils completely the initial requirements and the aim of the project.

3.2. Results for artificial paste samples

Table 4
Comparison results of $Ca(OH)_2$ content in simulated samples analyzed by the new chemical method and DTA method

Sample no.	Initial $Ca(OH)_2$ from DTA (%)	Cement paste—quartz by weight	Real $Ca(OH)_2$ content (%)	Measured $Ca(OH)_2$ from DTA (%)	Measured $Ca(OH)_2$ from the new method (%)
Sim1	4.30	1:4	0.86	–	1.16
Sim2	3.80	1:4	0.76	–	0.70
Sim4	3.60	1:9	0.36	–	0.31
Sim5	2.60	1:4	0.52	0.42	0.50
				0.42	0.52
Sim6	2.50	1:4	0.50	–	0.46
Sim9	0.80	1:4	0.16	–	0.18
Sim10	1.10	1:4	0.22	0.08	0.19
				0.13	0.21
		1:9	0.11	0.00	0.09
				0.00	0.10
				–	0.11

Because DTA analysis is a method which gives acceptable results for investigating $Ca(OH)_2$ content, especially for relatively high contents, artificial low-$Ca(OH)_2$ samples were made from the high-$Ca(OH)_2$-content samples, knowing the $Ca(OH)_2$ content from DTA testing. The known high-$Ca(OH)_2$-content samples were mixed with pure quartz powder and were used as the artificial low-$Ca(OH)_2$ samples in the analysis. The $Ca(OH)_2$ content of the artificial sample is calculated from the weight ratio of quartz to the original cement paste sample and $Ca(OH)_2$ content in that cement paste. Some of these artificial samples were also tested by DTA to compare the precision to the new titration method.

As mentioned previously, to get the very low $Ca(OH)_2$ samples used in the analysis, the artificial low-$Ca(OH)_2$ samples were made from the higher $Ca(OH)_2$ content cement paste (samples from Table 3) mixed with ground

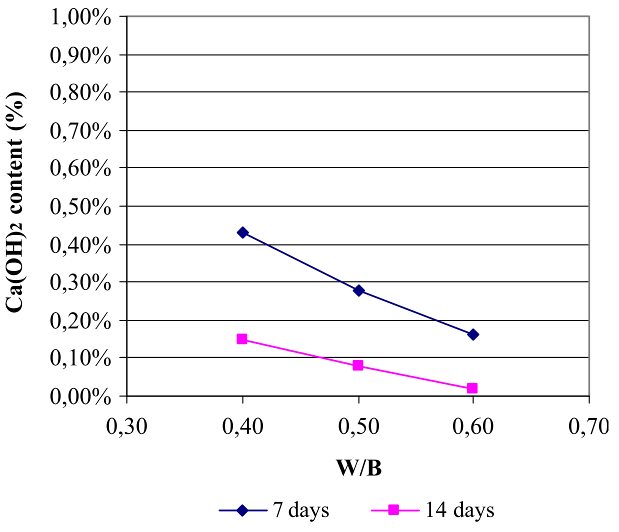

Fig. 1. $Ca(OH)_2$ content in high-slag-content cement paste with 50% fly ash replacement (DIN 1164-1: CEM III B) tested by the new chemical method.

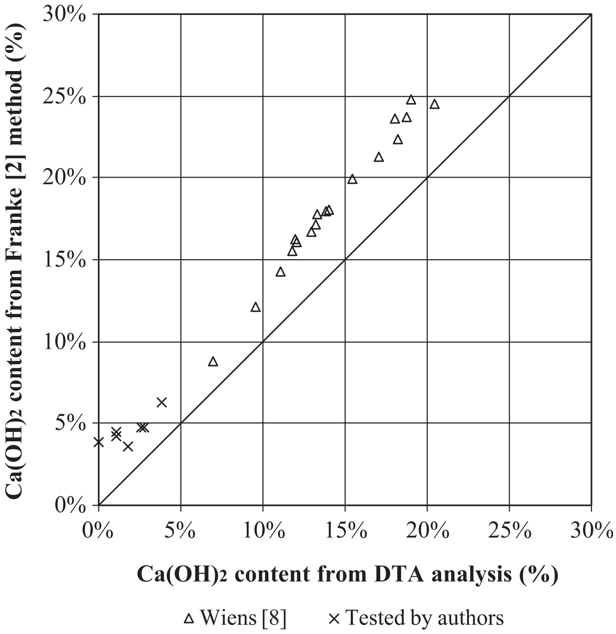

Fig. 2. Comparison of $Ca(OH)_2$ contents tested by DTA and Franke method.

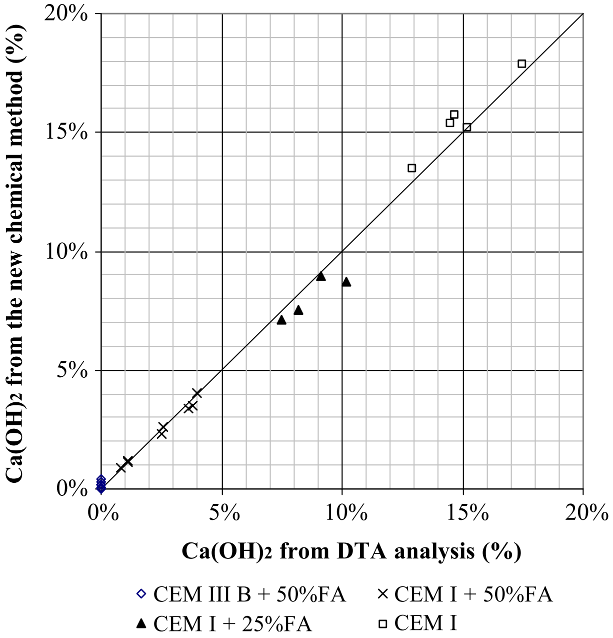

Fig. 3. Comparison of $Ca(OH)_2$ contents tested by DTA and the new chemical method.

pure quartz. Some samples have nearly 0% $Ca(OH)_2$ content. The results are demonstrated and are compared in Table 4. The results reveal that the new chemical method shows higher precision and accuracy in results than DTA analysis.

3.3. Results for all ranges of $Ca(OH)_2$-containing cement paste samples

In the present study, the performance of three testing methods: DTA analysis, Franke method [2], and our new chemical method are studied and compared. As shown in Fig. 2, the Franke method [2] always gives overestimated values for all ranges of $Ca(OH)_2$ content because the Franke [2] solution appears to attack some other hydrated mineral phases. The Franke [2] results are averagely about 20–100% and more beyond those of DTA analysis.

In Fig. 3, The amounts of $Ca(OH)_2$ investigated by the chemical method are compared with those of DTA method. It can be seen that the agreement between both methods is good (correlation is about .98). For most samples, the results from the chemical method and DTA method are comparable. However, as mentioned in previous sections, the new chemical method gives the better precision results in case of low-$Ca(OH)_2$-content sample, which is the major advantage of this new method.

4. Conclusion

The study proposes the new chemical method for dissolving and analyzing free $Ca(OH)_2$ content in cementing material. The benefit of the new chemical method is mainly expected on the testing of the very low $Ca(OH)_2$ content cement paste sample and mortar or concrete sample, which is beyond the capability of DTA analysis. The new extraction method deals with the instability of $Ca(OH)_2$ phases under appropriated pH conditions, in which $Ca(OH)_2$ is dissolved without other hydrated phases deterioration. However, because water-based solvent was used in extraction, the preliminary results obtained from the extraction are adjusted by the degree of hydration factor to eliminate the effect of further hydration during the dissolving process. The new method gives results comparable to the result from DTA analysis. However, the new method give more reliable results than DTA, in case of very low $Ca(OH)_2$ content analysis, both from simulated sample or pure poor $Ca(OH)_2$ paste sample, that would be very useful for mortar and concrete sample analysis. The results from the Franke method were always higher than of both DTA and the new chemical method.

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