

LEVEL OF CALCIUMHYDROXIDE AND
MECHANISMS OF CARBONATION IN HARDENED
BLENDED CEMENTS



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Synopsis

Pastes of blended cements have been investigated with respect to Ca(OH)_2 -content. Compared with a theoretically calculated Ca(OH)_2 -content, the experimental results show a relatively high level of Ca(OH)_2 , which indicates a silicarich C-S-H gel.

Further these blended cement pastes have been exposed to CO_2 , 60 % RH or 90 % RH. The results indicate a simultaneously carbonation of Ca(OH)_2 and C-S-H. For the pastes stored in 90 % RH, the Ca(OH)_2 shows a greater rate of carbonation compared with corresponding results from 60 % RH. In 60 % RH CO_2 , to a larger degree, seems to combine with C-S-H-gel.

Key words:

Blended cement pastes, content of calciumhydroxide, mechanism of carbonation.

(C = CaO , S = SiO_2 , H = H_2O)

1 INTRODUCTION

For some years it has been recognized that CO₂-attack on hardened cement paste has caused great damages to reinforced concrete because of reduction in Ca(OH)₂-content, and thereby loss of capability to protect concrete reinforcement bars against corrosion.

In addition the introduction of blended cements has led to concerns about an accelerated carbonation of concrete containing these cements because of their lower content of CaO compared with ordinary Portland Cement (OPC). The objective of the present study was to examine the level of Ca(OH)₂ in hardened pastes of blended cements, and to investigate alteration in pastes due to carbonation. Pastes of OPC were used as reference samples.

2 MATERIALS AND EXPERIMENTAL DETAILS

The cements were produced and delivered from NORCEM CEMENT A/S. The chemical composition of the cements according to the manufacturer is given in Table 1 together with the Blaine finenesses. Pastes were made of these cements using water/solid (w/s) ratios of 0.5 and 0.7. Samples with 5.0 % substitution of the cements with condensed silica fume, and one sample with 30.0 % silica fume substitution of OPC were also included in the experiments.

For determination of Ca(OH)₂ levels in hardened pastes, fresh mixtures were put into small polyethylene bottles, sealed, rotated for a couple of days, and then stored sealed for 6 months at room temperature.

For investigation of rate of carbonation and carbonation mechanism, pastes were mixed in a Hobart Mixer, put into 20 mm diameter polyethylene tubes, sealed, and rotated for the first days of hydration. After 3 months of hydration in sealed condition, the hardened pastes were cut into 40 mm long pieces. In order to expose only one cross section of the prisms to CO₂, they were covered with paraffin wax.

The samples were exposed to following four conditions:

0 % CO₂, 60 % RH, and 3 % CO₂, 60 % RH
0 % CO₂, 90 % RH, and 3 % CO₂, 90 % RH

Relative humidity was controlled by saturated salt-solutions. At selected intervals, samples were removed from the exposure chambers, depths of carbonation determined by use of phenolphthalein, whilst the outer 10 mm more thoroughly examined.

Table 1. Chemical Composition of the Cements

Type of cement	Loss on ignition %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	SO ₃ %	Undissolved residue %	K ₂ O %	Na ₂ O %	Alk. %	Un-bound CaO %	Blaine cm ² /g
OPC	1.41	20.20	5.00	3.24	62.87	2.28	3.30	0.35	1.13	0.36	1.10	0.78	3505
MP30 10 % fly ash	1.32	23.03	6.64	3.35	59.01	2.56	3.28	-	1.05	0.26	0.96	1.09	4015
MP30 25 % fly ash	0.62	28.25	11.13	3.61	50.23	2.28	2.81	-	0.95	0.35	0.97	1.26	4710

3 APPARATUS AND METHODS OF INVESTIGATION

The following methods and apparatus were used in the investigations:

- The content of chemically bound water and carbonates were followed by thermogravimetric analysis (TG) using a NETSCH 409 STA. The heating rate was 20°C/min. TG-sensitivity = 2 mg/cm, carrier gas = nitrogen.
- Changes in pore volume and pore size distribution were followed by He pycnometer and Hg intrusion, respectively. A Carlo Erba, Model 2000 with a maximum Hg pressure = 150 MPa was used.
- X-ray diffraction was carried out using a Philips PW 1710 diffractometer using CuK-alpha.
- Scanning electron microscopic (SEM) observation of the material was carried out using a JEOL JSM-T200.

4 RESULT AND DISCUSSION

4.1 Level of Ca(OH)_2

The Ca(OH)_2 content in the pastes after 6 months of hydration was determined/calculated from the TG-analysis. These results are given in Table 2 together with 2 theoretically calculated values. These calculations are done on assumption of mole fractions $\text{CaO}:\text{SiO}_2 = 0.8$ or 1.5 respectively in the calcium silicate hydrates.

Further the calculations are based upon the chemical compositions of the cements, the analyzed Ca(OH)_2 -level of the OPC-pastes, and the greater Blaine finenesses of the flyash cements have been taken into account.

As can be seen from the results, the blended cements show a relatively high level of Ca(OH)_2 . The analyzed Ca(OH)_2 -contents are very close to - or higher than a theoretical value based upon a mole fraction $\text{CaO}:\text{SiO}_2 = 0.8$ which means that silicarich calcium-silicate hydrates (C-S-H-phases) are formed in blended cementpastes. A silicarich C-S-H-phase was also detected from the thermodiagrams of the pastes containing 70 % OPC + 30 % silica fume /1/. The results also confirm with the investigations performed by M. Regourd /2/ on the composition of C-S-H-phases in OPC/-silica fume pastes. She found the Ca/Si ratio of C-S-H inversely proportional to the amount of silica fume.

Table 2. Analyzed and calculated Ca(OH)_2 -levels in blended cement pastes

Cement	Silica fume	w/s	Ca(OH)_2 ----- % Dried solid		
			Analyzed	Calculated $\text{CaO}:\text{SiO}_2 = 0.8$	Calculated $\text{CaO}:\text{SiO}_2 = 1.5$
OPC	0	0,5	21,4		
		0,7	24,1		
	5	0,5	14,8	15,7	11,7
		0,7	18,3	18,4	14,4
	30	0,5	2,2	0	0
		0,7	6,1	0	0
MP30 (10 % flyash)	0	0,5	18,0	17,2	13,0
		0,7	19,2	19,9	15,7
	5	0,5	12,9	11,9	3,8
		0,7	17,5	14,5	6,4
MP30 (25 % flyash)	0	0,5	12,1	11,0	0,4
		0,7	11,2	13,7	3,1
	5	0,5	8,8	5,9	0
		0,7	8,7	8,5	0

4.2 CO₂-attacks on hardened cement pastes

The reactions between CO₂ and the cement pastes were followed by thermogravimetric analyses (TG) of a 10 mm outer layer of the specimens. The results, expressed as weight ratio (CaCO₃/ignited solid), are shown in Fig 1 to Fig 4 and given in Table 3 for specimens exposed to 3 % CO₂ for twelve months.

Table 3. Content of CaCO₃ in specimens exposed to CO₂ for 12 months

$$\left(\frac{\text{CaCO}_3}{\text{ignited solid}} \right) \%$$

Cement	Silica Fume	v/s	60 % RH	90 % RH
OPC	0	0.5	59.9	49.8
		0.7	67.5	71.2
	5	0.5	47.4	47.4
		0.7	62.1	68.4
	30	0.5	35.5	6.8
		0.7	42.0	46.4
MP 30 (10 % flyash)	0	0.5	54.9	31.0
		0.7	60.9	67.1
	5	0.5	49.0	38.1
		0.7	54.0	65.0
MP30 (25 % flyash)	0	0.5	46.1	18.0
		0.7	48.0	55.8
	5	0.5	43.4	28.6
		0.7	65.5	51.1

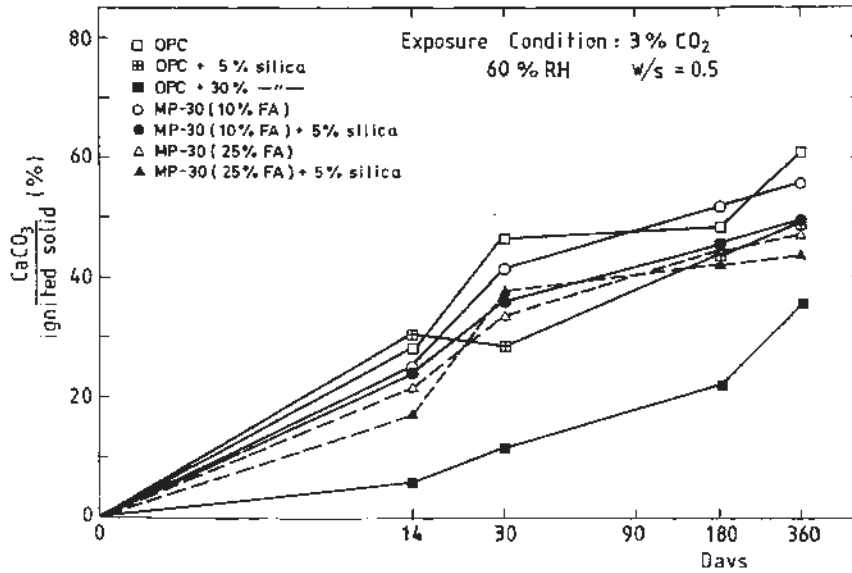


Fig 1. CaCO₃ in pastes water/solid = 0.5 exposed to 3 % CO₂, 60 % RH

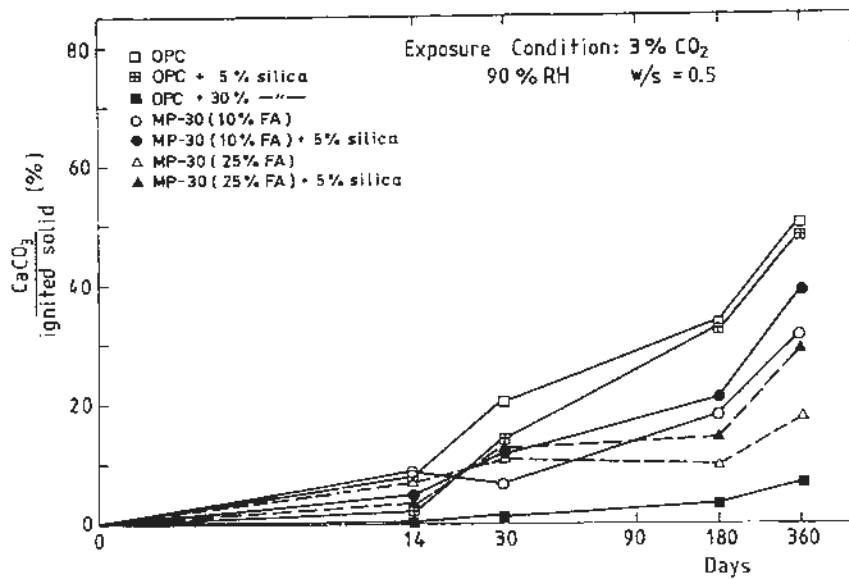


Fig 2. CaCO₃ in pastes water/solid = 0.5 exposed to 3 % CO₂, 90 % RH

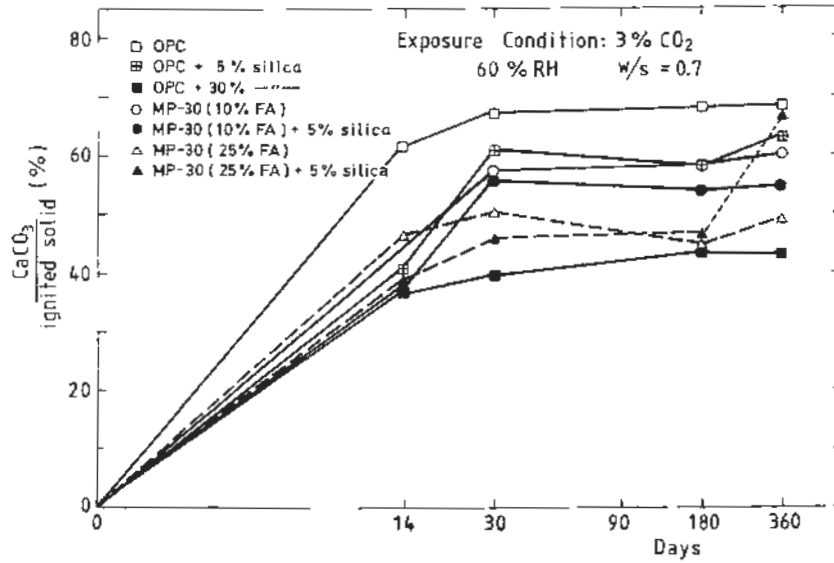


Fig 3. CaCO₃ in pastes, water/solid = 0.7, exposed to 3 % CO₂, 60 % RH

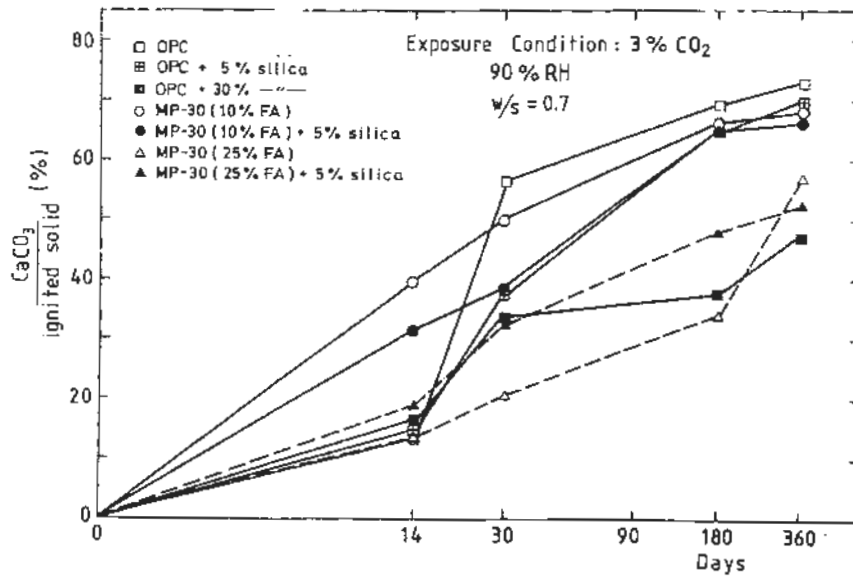


Fig 4. CaCO₃ in pastes water/solid = 0.7, exposed to 3 % CO₂, 90 % RH

From the results given in Table 3 and the figures it can be seen that the contents of CaCO₃ depends upon w/s ratio as well as the humidity in the exposure chamber. Pastes made with w/s = 0.7 show, as expected, a larger degree of carbonation than pastes made with w/s = 0.5. This is due to the more open structure of the specimens with w/s = 0.7, and thereby a greater surface available for CO₂-attacks. However, whereas pastes with w/s = 0.5 exhibit the larger content of carbonates when exposed to 60 % RH, the pastes with the more open structure, w/s = 0.7, from 90 days onwards showed the highest carbonate content at 90 % RH. These results have also been stated by other analytical methods like MIP, x-ray and SEM /3/.

4.3 Mechanism of carbonation

It was of interest to examine the observed larger content of carbonates in pastes stored in 90 % RH compared to those stored in 60 % RH.

A method reported by J. Kropp /4/ was followed.

Chemically bound water (= loss in weight from 120°C to 600°C on the TG-curves) was determined in cement pastes carbonated for one year and in the corresponding pastes stored at 0 % CO₂, in 60 % RH and 90 % RH respectively. This permitted the determination of dehydration of pastes due to carbonation as,

$$\Delta W = W_{(n.c.)} - W_{(c)}$$

where W = chemically bound water
 n.c. = not carbonated
 c = carbonated

and as one mol CO₂ gives one mol H₂O when Ca(OH)₂ carbonates, the molar ratio

$$\frac{\text{loss of water (mol)}}{\text{content of CO}_2 \text{ (mol)}}, \quad \left(\frac{-\text{H}_2\text{O mol}}{+\text{CO}_2 \text{ mol}} \right) \text{ has also been calculated.}$$

These results are shown in Fig 5 for the MP30 (10 % FA) paste, together with the content of calcium carbonate and chemically bound water of specimens stored at 0 % CO₂ and 3 % CO₂ respectively.

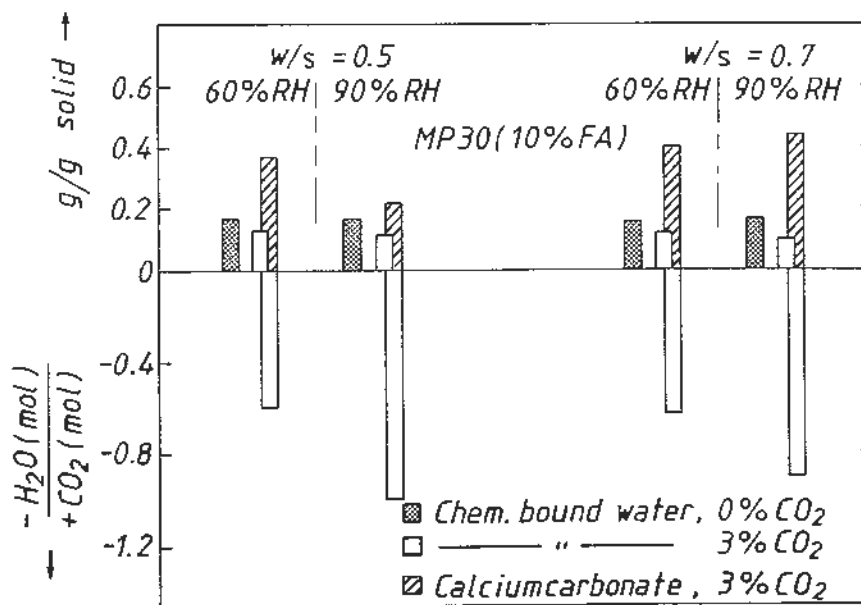


Fig 5. Chemically bound water, content of carbonates, and dehydration of chemically bound water vs CO₂ in a paste of 10 % fly ash cement

As can be seen from Fig 5 the dehydration pr mol CO_2 is greater for the samples stored at 90 % RH compared with 60 % RH. This is most pronounced for pastes made with $w/s = 0.5$ in spite of a much greater CaCO_3 -content in these samples when they have been stored at 60 % RH.

According to literature /5/, /6/, /7/ Ca(OH)_2 is the only mineral which set free water when it reacts with CO_2 . The results therefore indicate that Ca(OH)_2 reacts with CO_2 to a higher degree in 90 % RH compared with 60 % RH.

Unlike Ca(OH)_2 no water is released when C-S-H gel reacts with CO_2 /5/, /6/, /7/. The greater CaCO_3 content which was found in specimens stored in 60 % RH, therefore may be explained by a simultaneous carbonation of Ca(OH)_2 and C-S-H gel going on when pastes are exposed to CO_2 , and the mechanism of carbonation seems to be:

In 60 % RH, 3 % CO_2 , to a large degree, attacks the C-S-H phases. In 90 % RH, 3 % CO_2 primarily combines with Ca(OH)_2

According to J. Kropp /4/ this mechanism is most likely due to a solution of the CaCO_3 covering the surfaces of Ca(OH)_2 . This is caused by the relatively high humidity of the surroundings, here 90 % RH. Thereby new surfaces of Ca(OH)_2 will be available for CO_2 -attacks.

5 COMMENTS

As mentioned concerns have been expressed about an accelerated carbonation of concrete containing blended cements because of the lower Ca(OH)_2 content of these cements compared with OPC.

This investigation, however, has shown an unexpected high Ca(OH)_2 content in pastes of blended cements. See 4.1.

Further pastes of blended cements have due to the pozzolanic reaction a relatively high content of hydrated gel, which according to the reported results, combines with CO_2 . Thereby the hydrated gel will contribute in maintaining a relative high Ca(OH)_2 level. Therefore, an accelerated carbonation of Ca(OH)_2 in blended cements compared with OPC should not be expected if the humidity of the surrounding is about 60 % RH.

In an atmosphere with relative humidity of about 90 % RH, however, the Ca(OH)_2 content seems to be heavily reduced through a CO_2 attack. Because of the reduced Ca(OH)_2 level of blended cements compared with OPC an accelerated carbonation of blended cements may be expected in surroundings of high humidity.

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