HYDRATION OF THE CEMENT PASTE WITH Na₂CO₃ ADDITION

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Submitted April 4, 2000; accepted June 6, 2000.

This research provides a fundamental understanding of the early stage hydration of Portland cement paste modified by 2 and 4 wt.% of sodium carbonate. An excess of CO_3^2 - ions retards the $Ca(OH)_2$ development and enables an intensive rise and growth of $CaCO_3$ crystals in hydrated cement. This process lasts very intensively from 6 to 24 hours. A high conversion of unreacted clinker minerals to hydration products in the cement - Na_2CO_3 pastes takes place rapidly between 1 and 24 hours. Later the conversion of clinker minerals to the hydrate phase is reduced and higher contents of calcite and vaterite relative to that of $Ca(OH)_2$ in comparison with those found in the Portland cement paste are observed. As a consequence of this, differences in strength, dynamic modulus of elasticity and porosity between hardened Portland cement paste and those modified by Na_2CO_3 are found. The decrease in two-year compressive strength and elasticity modulus of cement - Na_2CO_3 pastes relative to Portland cement pastes is caused by the loss in binding capability due to preferential $CaCO_3$ formation at the early stage of cement hydration and consequent growth of $CaCO_3$ crystals due to gradual carbonation, particularly in air with 60 % of relative humidity. In this respect the higher volume of non-affected products of the hydration process by the action of CO_2 , the better compressive strength and elasticity modulus the cement paste becomes.

INTRODUCTION

In order to understand the chemistry of Portland cement hydration, it is necessary to consider the hydration processes of all its individual clinker minerals. The results have been interpreted to indicate the occurrence of three distinct stages in the course of hydration: *a*) the formation of a high CaO/SiO₂ low area intermediate, *b*) the conversion of this to a low CaO/SiO₂, high area intermediate and c) the conversion of this to stable hydration products [1-9].

Tricalciumisilicate (C_3S) is the major cementitious component of Portland cement. Its hydration reaction is represented by the following approximate chemical equation [10].

$$2Ca_3SiO_5 + 6H_2O \rightarrow Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2 \quad (1)$$

or in cement nomenclature

$$2C_3S + 6 H \rightarrow C_3S_2H_3 + 3CH$$

The products formed are a calcium silicate hydrate known as C-S-H and calcium hydroxide. The formula given for C-S-H is only a very rough approximation because also more than one variety of C-S-H is formed during the hydration reaction. Dicalciumsilicate (β -C₂S) hydrates much more slowly than C₃S does, to form similar type of C-S-H and Ca(OH)₂.

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7 \cdot 3H_2O + Ca(OH)_2 \quad (2)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$$

As for C₃S hydration, the formula given for C-S-H is also only roughly approximate. Hydrated C₃S is principal contributor to early compressive strength whereas β -C₂S to long-term compressive strength. Less calcium hydroxide is formed during β -C₂S hydration than when C₃S is hydrated, which has certain advantages to strength development [10].

Tricalciumaluminate (C₃A) hydrates very quickly to form C_2AH_8 and C_4AH_{13} which then convert with time to stable C_3AH_6 [10].

$$2Ca_{3}Al_{2}O_{6} + 21H_{2}O \rightarrow$$

$$\rightarrow Ca_{2}[Al(OH)_{5}]_{2} \cdot 3H_{2}O + 2[Ca_{2}Al(OH)_{7} \cdot 3H_{2}O]$$

$$\rightarrow 2\{Ca_{3}[Al(OH)_{6}]_{2}\} + 9H_{2}O$$
(3)

$$2C_{3}A + 21H \rightarrow$$

$$\rightarrow C_2 A H_8 + C_4 A H_{13} \rightarrow 2C_3 A H_6 + 9H$$

These immediately follow a reaction between the calcium sulphate in solution and the calcium aluminate hydrate to form ettringite $C_3A \cdot 3C\overline{S} \cdot H_{32}$.

 $\begin{array}{l} 2[\text{Ca}_2\text{Al}(\text{OH})_7 \ . \ 3\text{H}_2\text{O}] + 3\text{Ca}\text{SO}_4 \ . \ 2\text{H}_2\text{O} + 14\text{H}_2\text{O} \rightarrow \\ \rightarrow \text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \ . \ 26\text{H}_2\text{O} + \text{Ca}(\text{OH})_2 \end{array}$

$$C_4AH_{13} + 3C\overline{S}H_2 + 14H \rightarrow C_3A \cdot 3C\overline{S} \cdot H_{32} + CH \quad (4)$$

Calcium aluminoferrite is a solid solution within the $C_2A - C_2F$ system whose composition in Portland cements approximates to C_4AF . The C_4AF hydration is very similar to that of C_3A . Reaction is slower than for C_3A but increases with rising A/F ratio. C_3A and C_4AF contribute little to the strength of Portland cement paste. The indications are that carbon dioxide reacts principally with calcium hydroxide to form calcium carbonate. Other hydration products are capable of reacting under certain conditions [11 - 14]. The chemical reactions that characterise the carbonation are:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
(5)

This exothermic reaction reaction is accompanied by the heat evolution 2436 J per gram of reacted CaO (7.7 kJ mole⁻¹) [15]

$$C_3SH_3 + 3CO_2 \rightarrow 3CaCO_3 + S_2 + 3H_2O$$
(6)

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$
(7)

Some of the bicarbonate is washed out but some of the solution penetrates to combine with $Ca(OH)_2$ to form calcium carbonate.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$
(8)

For the carbonation of hydrated aluminates following formulae have been put forward [15]:

$$C_3AH + CO_2 \rightarrow CaCO_3 + hydrous A$$
 (9)

 $C_4AF + CO_2 \rightarrow CaCO_3 + hydrous A + hydrous F$ (10)

$$C_4AH_{13} + 4CO_2 \rightarrow 4CaCO_3 + 2 Al(OH)_3 + 10 H_2O(11)$$

An important aspect of these descriptions is the role of water in the reaction mechanisms. It has been observed that carbonation will not proceed at low relativity humidity levels [16 - 19].

Upon mixing with water Portland cement undergoes a five-stage sequence of microstructure formation during setting and hardening summarised thus [20 - 25]:

- 1. An immediate reaction with Ca²⁺ ions passing into solution.
- 2. A "dormant" period specified by a slow rise in Ca²⁺ ion concentration up to the supersaturating of the solution.
- 3. An accelerated period characterized by the formation of C-S-H deposits and rapid Ca(OH)₂ crystallisation
- 4. A deceleration period that is a consequence of formed hydrate phase layers with decreased porosity
- 5. Diffusion controlled hydration process due to decreased porosity and decreased transport of ionic species in the system.

An admixture accelerating hydration of clinker minerals may influence the setting. Sodium carbonate belongs to the group of soluble inorganic salts according to the classification of accelerating admixtures influencing mainly the acceleration of C_3S hydration [26]. Mechanism of the initial C₃S hydration in contact with carbonate has been explained already by follows [27 - 32]: a hydrate layer forming around the C₃S grain is after the contact with solution disintegrated by the excess of CO_3^2 ions. This results in markedly increased Ca²⁺ and OH⁻ diffusion velocity through the hydrate phase layer. A dormant period is shortened and the C₃S hydration is consequently accelerated. However this has a significant influence on pore structure development. Due to the excess of CO_3^{2-} ions at C_3S hydration amorphous CaCO3 particles are very quickly precipitated in the supersaturating solution of Ca²⁺ and CO_3^2 . In few minutes amorphous carbonate phase is transformed to CaCO₃ of crystalline nature. The results show that well crystallised calcite with residual amounts of amorphous calcite together with wellcrystallised vaterite are present in C₃S - carbonate system. The above carbonate phases together with carbonated C-S-H gel appear in hydrated C₃S carbonate system particularly at the ambient temperature and relative humidity (R.H.) of air 60 %.

Present paper is devoted to the study of the phase composition, porosity, strength and elasticity modulus development of Portland cement paste and those modified by 2 wt.% and 4 wt.% of Na₂CO₃ hydrated 1 hour to 720 days at various curing conditions.

EXPERIMENTAL PART

Materials

Portland cement (CEM I 42.5) and pure sodium carbonate Na_2CO_3 were used in the tests. The cement pastes were mixed with Portland cement to Na_2CO_3 ratio of 100 % / 0 % (control), 100 % / 2 % and 100 % / 4 % by weight and water to cement ratio of 0.5. Chemical composition, specific weight, specific surface area, setting characteristics and strength development of the cement are listed in table 1.

Experimental method

Cement pastes were prepared as prismatic specimens $20 \times 20 \times 120$ mm and cubes $20 \times 20 \times 20$ mm in steel moulds on a vibration table (50 Hz, 0.35 mm) with vibration time of 30 seconds. The specimens were stored 24 hours in a climate chamber at 20 °C and 100 % R. H., and subsequently at 20 $^{\circ}$ C / 100 % R. H. - wet cure for the next 27 days. Then they were divided into two groups and kept either in 20 °C / 100 % R. H. - wet air or 20 °C / 60 % R. H. - dry air for 365 days (cubes) and 720 days (prisms) respectively. After stopping the hydration with a mixture of acetone and ether and drying in a vacuum oven for 6 hours at 40 °C, the specimens were ground to the grain fineness \leq 90 µm. A dry powder was then stored in tightly closed test tubes maintained over anhydrous CaCl₂ filler in dessicator until required testing.

Cement pastes were tested on dynamic modulus of elasticity, flexural and compressive strength and total

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Chemical com	nposition (wt.%)	Mineralogical composition Bogue (wt.%)		
Insoluble residue	1.34	C ₃ S	36.08	
SiO ₂	21.90	C_2S	35.65	
Al ₂ O ₃	5.97	C ₃ A	11.43	
Fe ₂ O ₃	2.60	C_4AF	7.90	
CaO	61.87	3-days strength (MPa)	3.8 / 24.1	
MgO	1.51	28 - days strength (MPa)	6.1 / 41.4	
SO ₃	2.01	normal consistency (%)	29.0	
K ₂ O	1.19	initial set (hours/minutes)	2 / 55	
Na ₂ O	0.31	final set (hours/minutes)	4 / 05	
Ign. loss	1.21	specific gravity (kg m ⁻³)	3166	
CaO free	0.30	specific surface $(m^2 kg^{-1})$	343.4	

Table 1. Composition and basic properties of the cement.

porosity. To study the cement hydration X-ray diffraction patterns and thermal curves were made. Strength characteristics of the specimens were estimated according to EN 196 – 1 Standard [33]. Ultrasonic pulse velocities were measured on ultrasonic apparatus UNIPAN type 543. The dynamic modulus of elasticity (DME) values were calculated by the formula:

$$E_{\rm bu} = \rho_{\rm VD} \, . \, \gamma_{\rm L}^2 \, . \, 10^{-6} \tag{12}$$

where E_{bu} - DME (MPa), ρ_{VD} - volume density (kg m⁻³), γ_L^2 - impulse speed of longitudinal ultrasonic waves (m s⁻¹).

The volume density was estimated on the specimens of regular shape by weighting at calculated volume of tested prisms. The specific gravity was ascertained by a pycnometric method as the weight of the volume unit of solid constituents of the cement paste in powder stage. Total porosity was calculated on the basis of volume density and specific gravity values using the formula:

$$TP = \left(1 - \frac{\rho_{\rm VD}}{\rho_{\rm SG}}\right). \ 100 \tag{13}$$

where TP - total porosity as the content of pores and voids in the cement paste (%), ρ_{SG} - specific gravity (kg m^-3)

The percentage hydration was determined by a X-ray quantitative analysis at the Research Institute of Building Materials, Brno, Czech Republic. The content of Ca(OH)₂ was estimated by the sum of diffraction lines heights at 4.91 Å, 2.63 Å and 1.93 Å; of C₃S and β -C₂S at 2.77 Å and 2.78 Å; of calcite at 3.03 Å and 2.49 Å and of vaterite at 3.30 Å. The thermograms were recorded on Derivatograph Q 1500, MOM Budapest. In general, 200 mg of samples were heated at 10 °C per minute from 20 to 1 000 °C in air. The amount of bound water was determined from TG curves as the mass weight loss over the temperature range 100 - 450 °C ;

and of $Ca(OH)_2$ as the sum of mass weight loss over the temperature range 450 - 600 °C (endotherm corresponding to dehydroxylation of $Ca(OH)_2$) and beyond 800 °C (endotherm corresponding to decarbonation of $CaCO_3$).

RESULTS AND DISCUSSION

The percentage hydration of cement clinker minerals specified by bound water content as a function of time are plotted in figures 1 and 2. The explanation of the symbols inserted in figures 1, 2 and 3, 4, 8, 9, 10 is following: 1 - control - d, 2 wt.% Na₂CO₃ - d and 4 wt.% Na₂CO₃ - d: the control cement paste and those with 2 wt.% and 4 wt.% Na₂CO₃ addition cured in 20 °C / 60 % R. H. - dry air; 2 - control-w, 2 wt.% Na₂CO₃ - w and 4 wt.% Na₂CO₃ - w: the control cement paste and those with 2 wt.% and 4 wt.% Na_2CO_3 addition cured in 20 °C / 100 % R. H. - wet air. The time axes have been made logarithmic in all figures for the sake of convenient representation. The time of curing is given in hours except of figure 10 where the days are used. The time 672 hours and 8 760 hours is equal to 28 days and 365 days respectively.

The bound water content is 2.2 times higher in the paste with 4 wt.% of Na₂CO₃ relative to the control cement paste after 1-hour hydration. After 6 hours the content of bound water is 1.4 times higher in the paste with 2 wt.% of Na₂CO₃ and 1.5 times higher in the paste with 4 wt.% Na₂CO₃ compared to the control paste. With the time of exposure, the bound water content is higher in the control cement paste. The data for the content of free and total Ca(OH)₂ (figures 3, 4) obtained in the same pastes as reported in figures 1, 2 show that free and total Ca(OH)₂ formation does not follows the degree of hydration found for the gel-like hydration products. The calculations were corrected by CO_3^{2-} amount from Na₂CO₃. The formation of free and total Ca(OH)₂ is markedly influenced by the paste mixture composition. In time interval up to 24 hours of the hydration phase composition of cement pastes with

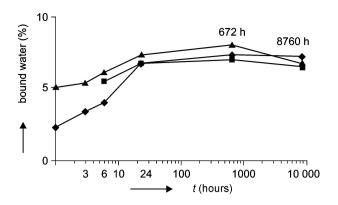


Figure 1. The bound water content in the cement pastes cured in 20 °C / 60 % R. H. - dry air.

◆ - control-d, ■ - 2 wt.% Na₂CO₃-d, ▲ - 4 wt.% Na₂CO₃-d

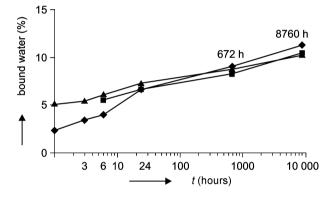


Figure 2. The bound water content in the cement pastes cured in 20 °C / 100 % R. H. - wet air.

 control-w, ■ - 2 wt.% Na₂CO₃-w, ▲ - 4 wt.% Na₂CO₃-w

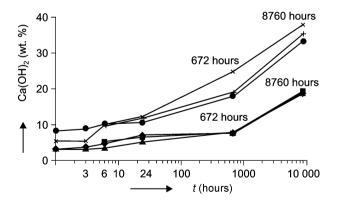


Figure 3. The Ca(OH)₂ content in the cement pastes cured in 20 °C / 60 % R. H. - dry air.

• - control-d (free), \blacksquare - 2 wt.% Na₂CO₃-d (free), • - 4 wt.% Na₂CO₃-d (free), × - control-d (total), - - 2 wt.% Na₂CO₃-d (total), • - 4 wt.% Na₂CO₃-d (total)

2 wt.% and 4 wt.% of Na_2CO_3 is characterised by reduced amount of $Ca(OH)_2$ and increased formation of

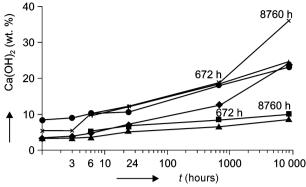


Figure 4. The Ca(OH)₂ content in the cement pastes cured in 20 °C / 100 % R. H. - wet air.

control-w (free), ■ - 2 wt.% Na₂CO₃-w (free),
 - 4 wt.% Na₂CO₃-w (free), × - control-w (total),
 - 2 wt.% Na₂CO₃-w (total),
 - 4 wt.% Na₂CO₃-w (total),

carbonates opposite to that in the control cement paste. After 24-hour hydration the curves cross each other indicating a marked mixture composition dependence on the phase composition development.

The above results are supported by phases detected from next thermoanalytical curves (figures 5, 6, 7). A preferential formation of the hydrate phase (endotherm at peak maximum of 120 °C corresponding to gel-like products dehydration) particularly in time of 1 and 6 hours in cement pastes with 2 wt.% and 4 wt.% of Na₂CO₃ relative to the control paste in figures 5, 6 and 7 is confirmed. On the contrary development of Ca(OH)₂ in the same time interval is slowed down. Free Ca²⁺ and CO₃²⁻ ions preferably react in the supersaturated solution firstly giving CaCO₃ nuclei that are later substituted to crystalline carbonates.

The curves in figures 8 and 9 show similar but not identical courses than those in figures 3 and 4. This is due to differences in evaluation principles of applied methods. The results evaluation from thermal analysis is based on thermal effects due to decomposition of reaction products in the cement paste. Contrary integration of the sums of diffraction lines heights is the principal evaluation method for percentage determination of the degree of cement hydration at X-ray quantitative analysis. After 6-hour hydration the curves showing percentage Ca(OH)₂ content cross each other. A suppressed Ca(OH)₂ formation in the control paste is immediately replaced by its rapid development relative to that in Na₂CO₃ modified cement pastes. In 20 °C / /100 % R. H. - wet cure the curves again cross each other clearly indicating a mixture composition dependence, and to a large extent a positive wet cure dependence on the Ca(OH)₂ formation in tested pastes.

Plots of $CaCO_3$ content as a function of the hydration time of cement pastes are shown in figures 8 and 9. There is an indication of markedly accelerated $CaCO_3$ formation in pastes with Na_2CO_3 at early stages of the hydration. The content of carbonation products is the least in the control paste after 365-day hydration in

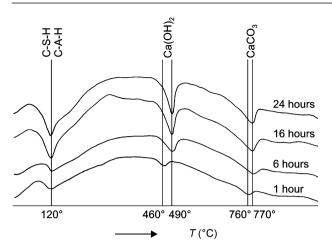


Figure 5. Thermograms of the control cement paste cured 1, 6, 16 and 24 hours at 20 °C and 100 % R. H. of air.

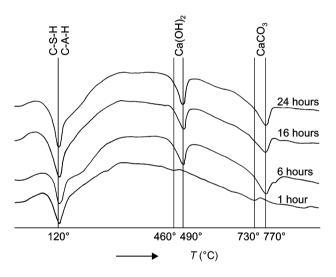


Figure 6. Thermograms of the cement paste with 2 wt.% of Na_2CO_3 cured 1, 6, 16 and 24 hours at 20 °C and 100 % R. H. of air.

both curing regimes. However experimental data indicate that the CaCO₃ content is higher in cement pastes cured in 20 °C / 60 % R. H. – dry air relative to those cured in 20 °C / 100 % R. H. – wet air. This shows a positive dry cure dependence on the carbonation products development.

The results have been interpreted to indicate the occurrence of two distinct stages in the course of hydration reactions of cement pastes with Na₂CO₃ addition. The first concerns the formation of gel-like hydration products with consequent microcrystalline Ca(OH)₂ particle development. High-lime products of the hydration process are unstable with the respect to its surroundings due to the excess of CO_3^2 ions in the pore solution and quickly are transformed to calcite and vaterite. This process lasts very intensively up to 24 hours of the hydration, and then in a slower rate up to the 28th day of curing.

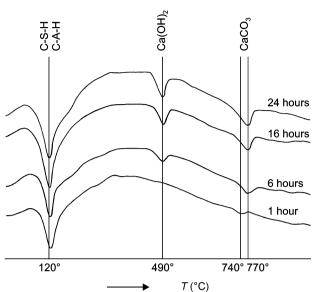


Figure 7. Thermograms of the cement paste with 4 wt.% of Na_2CO_3 cured 1, 6, 16 and 24 hours at 20 °C and 100 % R. H. of air.

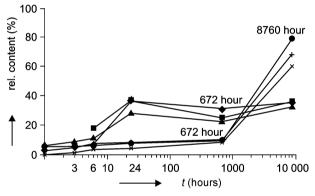
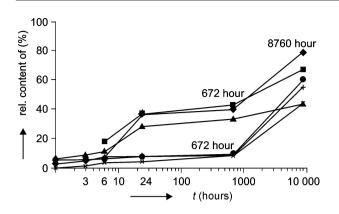


Figure 8. Relative content of $Ca(OH)_2$ and $CaCO_3$ in the cement pastes cured in 20 °C / 60 % R. H. - dry air.

◆ - control-d (Ca(OH)₂), ■ - 2 wt.% Na₂CO₃-d (Ca(OH)₂), ▲ - 4 wt.% Na₂CO₃-d (Ca(OH)₂), × - control-d (CaCO₃), - 2 wt.% Na₂CO₃-d (CaCO₃), ● - 4 wt.% Na₂CO₃-d (CaCO₃)

In the second stage of the hydration process carbonation initiated by the excess of CO_3^2 ions at early stage of hydration in cement pastes with Na₂CO₃ is more intense in comparison with that in the control cement paste in each followed time interval. A dense, well – developed network of CaCO₃ crystalline nuclei in the pore solution of Na₂CO₃ modified cement pastes at early stage of hydration results in a progressive formation of CaCO₃ crystals per unit volume of hydrated cement paste capable of gradual reacting with atmospheric CO₂. The velocity of carbonation reaction and the volume of developed carbonation products are higher in Na₂CO₃ modified cement pastes relative to the control paste.



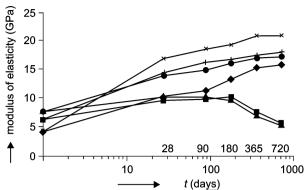


Figure 9. Relative content of Ca(OH)₂ and CaCO₃ in the cement pastes cured in 20 °C / 100 % R. H. - wet air. ◆ - control-w (Ca(OH)₂), ■ - 2 wt.% Na₂CO₃-w (Ca(OH)₂), ▲ - 4 wt.% Na₂CO₃-w (Ca(OH)₂), × - control-w (CaCO₃), - - 2 wt.% Na₂CO₃-w (CaCO₃), ● - 4 wt.% Na₂CO₃-w (CaCO₃)

Figure 10. Changes in dynamic modulus of elasticity of tested specimens.

• - control-d, ■ - 2 wt.% Na₂CO₃-d, ▲ - 4 wt.% Na₂CO₃-d,
× - control-w, - - 2 wt.% Na₂CO₃-w, ● - 4 wt.% Na₂CO₃-w

Table 2. Specific gravity and volume density and porosity of cement pastes cured in dry (D) or wet (W) air.

		hydration of cement pastes in time					
type of cement paste	property of the cement paste at $w/c = 0.5$	6 h W	24 h W	28 days D	28 days W	365 days D	365 days W
pusie							
sp vo	compressive strength (MPa)		1.8	10.4	19.7	23.6	32.6
	specific gravity (g cm ⁻³)		2.742	2.592	2.269	2.588	2.248
	volume density (g cm ⁻³)		1.366	1.476	1.398	1.548	1.549
	porosity (vol.%)		50.17	42.67	38.27	40.18	31.10
with -	compressive strength (MPa)	0	3.3	9.8	15.5	16.9	23.0
admixture	specific gravity (g cm ⁻³)	2.735	2.732	2.547	2.257	2.708	2.493
of 2 wt.%	volume density (g cm ⁻³)	1.222	1.343	1.464	1.336	1.571	1.452
Na ₂ CO ₃	porosity (vol.%)	55.34	50.86	42.79	40.86	41.96	41.75
with	compressive strength (MPa)	0.2	4.3	11.3	11.6	10.6	17.6
admixture	specific gravity (g cm ⁻³)	2.803	2.704	2.521	2.256	2.605	2.439
of 4 wt.%	volume density (g cm ⁻³)	1.370	1.316	1.422	1.370	1.457	1.443
Na_2CO_3	porosity (vol.%)	51.13	51.30	43.60	39.29	44.10	40.86

Table 3. Flexural and compressive strength, dynamic modulus of elasticity of cement pastes kept 720 days in dry (D) and wet (W) air.

cement	curing	streng	elasticity modulus		
paste		flexural	compressive	(GPa)	
control	D	2.4	24.3	15.7	
	W	4.7	30.0	20.7	
2 wt.% Na ₂ CO ₃	D	1.1	18.9	5.6	
	W	3.2	22.2	17.9	
4 wt.% Na ₂ CO ₃	D	0.75	11.9	5.3	
	W	2.3	19.5	17.1	

Bearing in the mind a previous discussion on proposed hydration mechanism in the Na₂CO₃ modified cement pastes characterised by a preferential carbonation of the bonding hydrate phase the results given in table 2 offer a real picture of the dependence between the paste mixture composition and important engineering properties. With time of hydration compressive strength is markedly increased while total porosity is pronouncedly decreased in the control cement paste relative to those found in the pastes with 2 and 4 wt.% of Na₂CO₃. The higher percentage of Na₂CO₃ dosage, the higher negative influence on strength and total porosity developments of cement pastes with Na₂CO₃ addition.

This is confirmed by the results shown in table 3 and figure 10. An evident loss in compressive strength and dynamic modulus of elasticity in cement pastes with Na₂CO₃ addition relative to the control paste was observed, particularly in the specimens kept for 720 days in 20 °C / 60 % R.H. – dry air. The loss in long-term compressive strength and dynamic modulus of elasticity are typical symptoms of carbonation reaction initiated by Na₂CO₃ addition to the cement, especially at 60 % R.H. and temperature of 20 °C.

CONCLUSIONS

- 1. The rate of carbonation depends upon environmental moisture conditions. A lower rate of carbonation occurs in cement pastes cured in wet air. Such specimens are more immune from the consequences thereof than those exposed to dry air.
- 2. The rate of carbonation of Na₂CO₃ modified cement pastes is progressively accelerated in each time interval due to the excess of CO₃² ions in paste mixture composition at early stage of hydration relative to that of control cement paste. A destructive effect of carbonation is evidently demonstrated by decreased compressive strength and dynamic modulus of elasticity values and increased total porosity in Na₂CO₃ modified cement pastes relative to those in control specimens cured 720 days in dry and wet air.
- 3. Mechanism of carbonation reaction of Na₂CO₃ modified cement pastes should be seen distinctly distinguished in two separate stages. The first stage is concerned by the preferable formation of products of the hydration process, which are unstable with the respect to its surroundings, and quickly are transformed to the carbonation phases. This stage lasts 28 days but a decisive significance have the first 24 hours. The second stage is characterised by the loss in binding capability due to gradual carbonation. The rate of the decrease of strength and modulus of elasticity for Na₂CO₃ cement pastes is much greater than that for control cement pastes in each time of dry or wet curing.

Acknowledgement

The author wishes to thank the Slovak Grant Agency VEGA (grant: 2/5105/20) for its support toward this work.

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Submitted in English by the author.

HYDRATÁCIA CEMENTOVEJ KAŠE S PRÍSADOU NA₂CO₃

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Prešetroval sa priebeh hydratácie cementu a zisťovali sa zmeny v celkovej pórovitosti, dynamickom module pružnosti a pevnosti v tlaku kaše z Portlandského cementu a kaší s prísadou 2 hmotn.% a 4 hmotn.% Na₂CO₃ zhotovených s vodným súčiniteľom 0,5 v čase od 1 hodiny do 720 dní. Skúšobné

vzorky sa ošetrovali 24 hodín pri teplote 20 °C a 100% relatívnej vlhkosti vzduchu, neskôr buď v rovnakom úložnom prostredí alebo vo vzduchu s relatívnou vlhkosťou vzduchu iba 60%.

Rýchlosť karbonatácie cementových kaší s prísadou Na₂CO₃ sa významne urýchľuje v dôsledku nadbytku CO₃²⁻ iónov v objemovej jednotke cementovej kaše v počiatočnej fáze hydratácie cementu. Mechanizmus karbonatačnej reakcie v cementových kašiach s prísadou Na₂CO₃ charakterizujú dve zreteľne odlíšiteľné etapy. V prvej etape sa rozhodujúcim spôsobom uplatňuje chemický proces premeny vzniknutých nestabilných produktov hydratácie cementu s vysokým obsahom viazanej vody a viazaného CO₂, a portlanditu na CaCO3 fázy. Rýchla konverzia väzných hydratačných produktov a portlanditu na karbonáty prebieha extrémne rýchlo počas 24 hodín hydratácie cementu a neskôr menej intenzívne až do 28. dňa veku skúšobných vzoriek. Tento chemický proces je úzko spätý s tvorbou vysokopórovitej mikroštruktúry cementových kaší s prísadou Na2CO3 v časovom intervale 1 až 28 dní v obidvoch úložných prostrediach.

V druhej etape sa prejavuje deštrukčný účinok karbonatácie evidentnou stratou na hodnotách dynamického modulu pružnosti a pevnosti v tlaku skúšobných vzoriek, čo úzko súvisí na čase evidentne závislým a významným zhoršovaním pórovitosti cementových kaší s prídavkom uhličitanu sodného. Faktorom determinujúcim rýchlosť karbonatácie a s ňou súvisiacu mechanickú degradáciu skúšobných vzoriek sa v tejto etape stáva difúzia atmosferického CO_2 dovnútra zatvrdnutých cementových kaší v závislosti na v nich vytvorenej pórovej štruktúre. V porovnávacej cementovej kaši s mikroštruktúrou a celkovou pórovitosťou vyvinutou bez vplyvu prísady sa v čase nezistila žiadna mechanická degradácia.

Dosiahnutý stupeň karbonatácie rozhodujúco závisí od vonkajších podmienok ošetrovania v každom časovom momente po 24 hodinách počiatočnej hydratácie kaší vo vlhkom vzduchu. Nižší stupeň karbonatácie sa preukázal vo všetkých cementových kašiach trvalo ošetrovaných vo vlhkom vzduchu v porovnaní s tými uloženými v suchom prostredí.