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DEGREE OF HYDRATION IN CEMENT PASTE AND C_3A–SODIUM CARBONATE–WATER SYSTEMS

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This research provides a fundamental understanding of the early stage hydration of Portland cement paste, tricalcium aluminate (C_3A) paste at water to cement ratio of 0.5 and C_3A suspension at water to cement ratio of 5.0 modified by 2 or 4 mass% of sodium carbonate. A high conversion of unreacted clinker minerals to gel-like hydration products in the cement–Na_2CO_3 pastes takes place rapidly between 1st to 24th h. Contrary the $Ca(OH)_2$ formation within the same time interval is retarded in the excess of CO_3^{2-} ions due to intensive rise and growth of $CaCO_3$ crystals in hydrated cement. 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 a decrease in strength and an increase in porosity between hardened Portland cement paste without sodium carbonate and those modified by Na_2CO_3 are observed. C_3A hydrates very quickly with sodium carbonate between 1st and 24th h forming hydration products rich in bound water and characterized also by complex salts of $(x)C_3A\cdot(y)CO_2\cdot(z)H_2O$ type, whereas C_3A–H_2O system offers C_3AH_6 as the main hydration product. Higher content of the formed calcium aluminate hydrates in C_3A–Na_2CO_3–H_2O system also contributes to early strength increase of Portland cement paste.

Keywords: *C_3A suspension, cement paste, hydration, porosity, strength*

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 of Portland cement, and mainly tri- and dicalcium silicates: (a) the formation of a high CaO/SiO_2 low area intermediate, (b) the conversion of this to a low CaO/SiO_2, high area intermediate and (c) the conversion of this to stable hydration products [1–9].

Tricalciumsilicate (C_3S) is the major 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

$$2C_3S+6H\rightarrow C\text{–}S\text{–}H+3CH$$

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-C_2S) hydrates much more slowly than C_3S does, to form similar type of C–S–H and $Ca(OH)_2$.

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

$$2C_2S+4H\rightarrow C\text{–}S\text{–}H+CH$$

Hydrated C_3S is a principal contributor to early compressive strength whereas β-C_2S contributes to long-term strength. Less calcium hydroxide is formed during β-C_2S hydration than when C_3S is hydrated, which has certain advantages to strength development [10].

Tricalciumaluminate (C_3A) normally occurs in Portland cement clinker between 5 to 15% by mass and hydrates very quickly in water to form hexagonal plate hydrates of C_2AH_8 and C_4AH_{13} in the first instance which convert with time to the more stable cubic C_3AH_6, or if the temperature is sufficiently high (>40°C), C_3A converts directly to C_3AH_6.

$$\begin{gathered}2Ca_3Al_2O_6+21H_2O\rightarrow\\ Ca_2[Al(OH)_5]_2\cdot 3H_2O+2[Ca_2Al(OH)_7\cdot 3H_2O]\rightarrow\\ 2(Ca_3[Al(OH)_6]_2)+9H_2O \quad (3)\end{gathered}$$

$$2C_3A+21H\rightarrow C_2AH_8+C_4AH_{13}\rightarrow 2C_3AH_6+9H$$

These immediately follow in Portland cement a reaction between the calcium sulphate in solution and

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the calcium aluminate hydrate to form ettringite $C_3A\cdot 3C\overline{S}\cdot H_{32}$.

$$2[Ca_2Al(OH)_7\cdot 3H_2O]+3CaSO_4\cdot 2H_2O+14H_2O\rightarrow Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O+Ca(OH)_2 \quad (4)$$

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

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_4AF contributes 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 characterize the carbonation are:

$$Ca(OH)_2+CO_2\rightarrow CaCO_3+H_2O+q \text{ calories} \quad (5)$$

where q=580 calories per gram of reacted CaO (=7.7 kJ mol^{-1}) [15]

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

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

The degree of carbonation of C–S–H gel increases with the following parameters:

(a) reaction temperature, (b) specific surface area of the particles, (c) time of aeration, (d) relative humidity of the reacting environment and (e) partial pressure of carbon dioxide [15].

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

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

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 [16]. Mechanism of the initial C_3S hydration in contact with carbonate has been explained already by follows [17–22]: a hydrate layer forming around the C_3S grain is after the contact with solution disintegrated by the excess of CO_3^{2-} ions. This results in markedly increased Ca^{2+} and OH^- diffusion velocity through the hydrate phase layer. A dormant period is shortened and the C_3S 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 $CaCO_3$ particles are very quickly precipitated in the supersaturating solution of Ca^{2+} and CO_3^{2-}. In few minutes amorphous carbonate phase is transformed to $CaCO_3$ of crystalline nature. The results show that well crystallized calcite with residual amounts of amorphous calcite together with well-crystallized vaterite is present in hydrated C_3S–carbonate system. The above carbonate phases together with carbonated C–S–H gel appear in hydrated C_3S–carbonate system particularly at the ambient temperature and relative humidity 60%.

For ultimate carbonation of hydrated calcium aluminates following formulae have been put forward [23]:

$$C_3AH_6+CO_2\rightarrow CaCO_3+\text{hydrous } Al_2O_3 \quad (9)$$

$$C_3(A,F)H_6+CO_2\rightarrow CaCO_3+\text{hydrous } Al_2O_3+\text{hydrous } Fe_2O_3 \quad (10)$$

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

Early carbonation of hydrated C_3A and C_2A–C_2F system results in the initial formation of hexagonal plate and hexagonal prism type phases of $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O(C_3A\cdot Cc\cdot H_{11})$ and $3CaO\cdot Al_2O_3\cdot 3CaCO_3\cdot 30H_2O(C_3A\cdot 3Cc\cdot H_{30})$; $3CaO\cdot(Al_2O_3\cdot Fe_2O_3)\cdot CaCO_3\cdot 11H_2O\{C_3\cdot(A.F)\cdot Cc\cdot H_{11}\}$ and $3CaO\cdot(Al_2O_3\cdot Fe_2O_3)\cdot 3CaCO_3\cdot 30H_2O\{C_3\cdot(A.F)\cdot 3Cc\cdot H_{30}\}$, respectively. Contemporarily a surface zone of hemicarbonate $C_4A\cdot 1/2CO_2\cdot 12H_2O$ on the crystals of C_4AH_{13} and C_4AH_{19} is formed. At temperature of 20°C the monocarboaluminate hydrates tend to be more stable forms than tricarboaluminate hydrates becoming stable at lower temperatures [24]. Formation of the monocarboaluminate hydrate from C_3A and $CaCO_3$ is very rapid. Ultimately these hydrates are further attacked by CO_2 to form calcium carbonate and aluminate gel or gibbsite [25].

This paper is concerned by the hydration of Portland cement and C_3A and the study of the formed phase compositions both of the systems as well as strength and porosity development of Portland cement paste and those modified by 2 or 4 mass% of Na_2CO_3 hydrated for 1 h to 365 days in various curing conditions.

Experimental

Materials

Portland cement (CEM I 42.5), pure tricalcium aluminate (C_3A) and sodium carbonate Na_2CO_3 were used in these experiments. The cement pastes were prepared with Portland cement and Na_2CO_3 at ratio of 100–0% (control), 100–2% and 100–4% by mass at water to cement ratio of 0.5. C_3A was mixed with 4 mass% of Na_2CO_3 at water to cement ratio either of 0.5 (comparison with Portland cement pastes) or 5.0 for C_3A–H_2O suspensions (comparison with C_3A pastes). Chemical composition, specific mass, specific surface area, setting characteristics and strength

Table 1 Composition and basic properties of the cement

Chemical composition/%		Mineralogical composition Bogue%	
Insoluble residue	1.34	C_3S	36.08
SiO_2	21.90	C_2S	35.65
Al_2O_3	5.97	C_3A	11.43
Fe_2O_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_2O	1.19	Initial set/hours-minutes	2–55
Na_2O	0.31	Final set/hours-minutes	4–05
Ignition loss	1.21	Specific gravity/kg m^{-3}	3166
CaO free	0.30	Specific surface/m^2 kg^{-1}	343.4

development of the cement are listed in Table 1. To prepare $3CaO\cdot Al_2O_3$ (C_3A), 50 g of raw materials in predetermined proportions were taken and ball milled for 60 min for homogenization. The powder was dried overnight in a hot air oven at 100°C and then fired in an electric muffle furnace. The firing temperature was kept at 1250°C for three hours using a heating rate approximately 200°C h^{-1}. The clinkered product was left to cool overnight to the room temperature and then grounded and sieved through 63 μm meshes. After firing, C_3A was put into a glass tube to avoid moistening and carbonation from air.

Methods

Cement pastes were prepared as cubes 20·20·20 mm in steel moulds on a vibration table (50 Hz, 0.35 mm) with vibration time of 30 sec. The specimens were stored up to 24 h in a climate chamber at 20°C and 100% R. H., and subsequently at 20°C/100% R. H. – wet cure for the next 27 days. They were then 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. After stopping the hydration with a mixture of acetone and ether and drying in a vacuum oven for 6 h at 40°C, the specimens were grinded to the grain fineness ≤90 μm. A dry powder was then stored in tightly closed test tubes maintained over anhydrous $CaCl_2$ filler in desiccators until testing.

C_3A pastes and suspensions were prepared by manual mixing. The pastes were stored for 24 h in a climate chamber at 20°C and 100% R. H., and subsequently were kept in 20°C/100% R. H. – wet air for the next 27 days. The suspensions were maintained in polyethylene beakers and left to a gentle, slow mixing in water at 20°C for 24 h. Hydration was stopped by the same way as that of the cement pastes. A dry powder of hydrated C_3A after sieving through 63 μm meshes was kept in tightly closed test tubes over anhydrous $CaCl_2$ filler in desiccators until testing.

Cement pastes were tested for compressive strength and total porosity. To study the cement hydration, X-ray diffraction patterns and thermal curves were observed. Strength characteristics of the specimens were estimated according to EN 196–1 Standard [26].

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:

$$TP=\left(1-\frac{\rho_{VD}}{\rho_{SG}}\right)\cdot 100 \qquad (12)$$

where *TP* is total porosity as the content of pores and voids in the cement paste, % ρ_{SG} is specific gravity, kg m^{-3}, ρ_{VD} is volume density, kg m^{-3}.

The percentage hydration was determined by an X-ray quantitative analysis at the Research Institute of Building Materials, Brno, CZ. The content of $Ca(OH)_2$ was estimated by the sum of diffraction lines heights at 0.491, 0.263 and 0.193 nm; of C_3S and β-C_2S at 0.277 and 0.278 nm, respectively, of calcite at 0.303 and 0.249 nm and that of vaterite at 0.330 nm. To study C_3A hydration X-ray diffraction patterns were recorded using Philips apparatus, CuK_α radiation and Ni-filter. Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted from 20 to 1000°C using a Derivatograph Q 1500, MOM Budapest. The sample mass was 20 mg and heating rate 10°C min^{-1} in flowing air. The amount of bound water was determined from TG curves as the mass loss over the temperature range 100–450°C ; and of $Ca(OH)_2$ as the sum of mass loss over the temperature range 450–600°C {endotherm corresponding to dehydroxylation of $Ca(OH)_2$ indicating free portlandite} and beyond 800°C {endotherm corresponding to decarbonation of $CaCO_3$ indicating total $Ca(OH)_2$, free and carbonated altogether}.

Results and discussion

The percentage hydration of cement clinker minerals specified by bound water content as a function of time is plotted in Figs 1 and 2. The explanation of the symbols inserted in Figs 1 and 4 is as follows: Fig. 1 – control – d, 2 mass% Na_2CO_3 – d and 4 mass% Na_2CO_3 – d. The control cement paste and those with 2 and 4 mass% of Na_2CO_3 addition cured in 20°C/60% R. H. – dry air; Fig. 2 – control-w, 2 mass% Na_2CO_3 – w and 4 mass% Na_2CO_3 – w. The control cement paste and those with 2 and 4 mass% of Na_2CO_3 addition were 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 h: 672 and 8760 h, which correspond to 28 and 365 days, respectively.

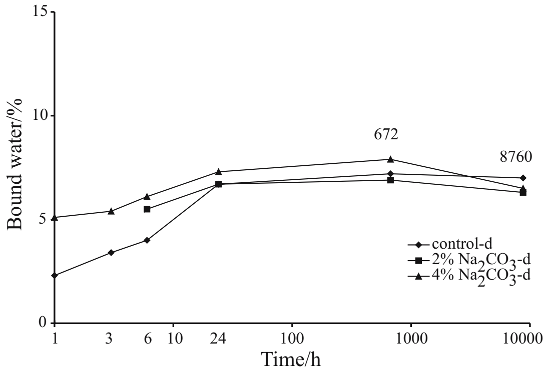

Fig. 1 The bound water content in the cement pastes cured in 20°C/60% R. H. – dry air

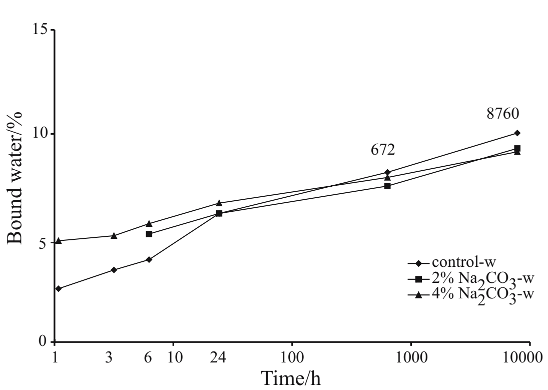

Fig. 2 The bound water content in the cement pastes cured in 20°C/100% R. H. – wet air

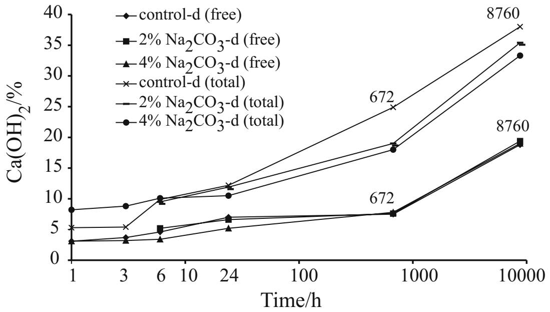

Fig. 3 The $Ca(OH)_2$ content in the cement pastes cured in 20°C/60% R. H. – dry air

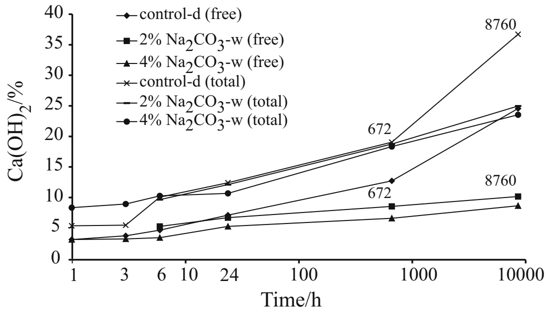

Fig. 4 The $Ca(OH)_2$ content in the cement pastes cured in 20°C/100% R. H. – wet air

The bound water content is 2.2 times higher in the paste with 4 mass% of Na_2CO_3 relative to the control cement paste after 1 h hydration. After 6 h the content of bound water is 1.4 times higher in the paste with 2 mass% of Na_2CO_3 and 1.5 times higher in the paste with 4 mass% of Na_2CO_3 compared to the control paste. With exposure time, the bound water content is higher in the control cement paste. The data for the content of free and total $Ca(OH)_2$ (Figs 3, 4) obtained in the same pastes as reported in Figs 1, 2 show that free and total $Ca(OH)_2$ formation does not follow the degree of hydration found for the gel-like hydration products. The calculations were corrected by CO_3^{2-} amount from Na_2CO_3. The formation of free and total $Ca(OH)_2$ is markedly influenced by the paste mixture composition. In time interval up to 24 h of hydration, phase composition of cement pastes with 2 and 4 mass% of Na_2CO_3 is characterized by reduced amount of $Ca(OH)_2$ and increased formation of carbonates opposite to that in the control cement paste. The curves cross each other after 24 h hydration indicating a marked mixture composition dependence on the phase composition development.

The above results are supported by phases detected from DTA plots (Figs 5, 6, 7). A preferential formation of the hydrate phase of type C–S–H and C–A–H (endotherm at peak maximum of 120°C corresponding to the above gel-like hydration products) particularly in time of 1 and 6 h in cement pastes with 2 and 4 mass% of Na_2CO_3 relative to the control paste

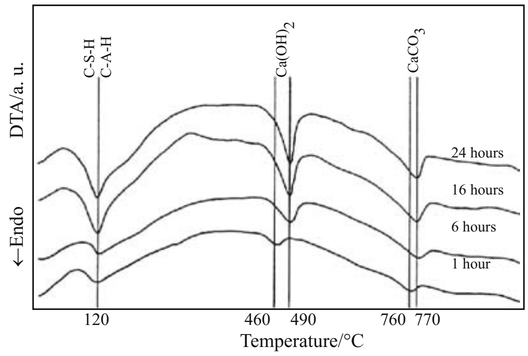

Fig. 5 DTA curves of the control cement paste cured for 1, 6, 16 and 24 h at 20°C/100% R. H. – wet air

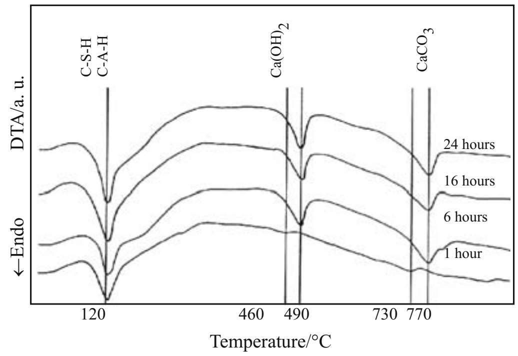

Fig. 6 DTA curves of the cement paste with 2 mass% of Na_2CO_3 cured for 1, 6, 16 and 24 h in 20°C/100% R. H. – wet air

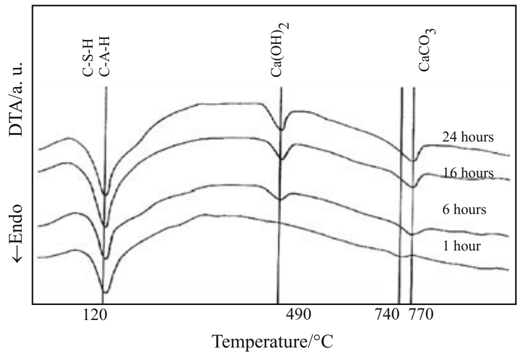

Fig. 7 DTA curves of the cement paste with 4 mass% of Na_2CO_3 cured for 1, 6, 16 and 24 h at 20°C/100% R. H. – wet air

is confirmed. Contrary, development of $Ca(OH)_2$ in the same time interval is slowed down. The addition of Na_2CO_3 accelerates formation of gel-like hydration products when compared to crystalline $Ca(OH)_2$ development. This results in more rapid strength growth at early stage hydration of the cement paste. Free Ca^{2+} and CO_3^{2-} ions preferably react in the supersaturated solution firstly giving $CaCO_3$ nuclei that are later substituted to crystalline carbonates, also contributing to strength increment at early stage hydration. It is believed that besides C_3S and β-C_2S hydration, the further clinker mineral contributing to strength increase at early stage hydration is tricalcium aluminate. C_3A gives a variety of quickly formed aluminate hydrates influencing microstructure development of the Portland cement paste. Bearing in mind that C_3A content in Portland cement is between 5 and 12 mass% generally, one would not disappreciate its role on the hydration rate and growth of early strengths in the cement. For this aim mineralogical composition of hydrated C_3A systems was studied in more detail. X-ray diffractograms of origin unhydrated C_3A and C_3A pastes with and without Na_2CO_3 addition after 24 h hydration in 20°C/100% R. H. – wet air are displayed in Fig. 8. C_3A is characterized by diffraction lines at 0.404, 0.267, 0.219 and 0.190 nm. Modification of C_3A with water leads to significant structural changes. The phase analysis shows that besides reflections of unhydrated C_3A peaks of calcium aluminate hydrates are present. The main hydration product is tricalcium aluminate-6 hydrate (C_3AH_6) as proved by the reference of peaks at 0.509, 0.333, 0.312, 0.228 and 0.203 nm. Dicalcium aluminate – 8 hydrate (β-C_2AH_8 recognized by the reflection at 1.03 nm), tetracalcium aluminate – 19 hydrate (C_4AH_{19} confirmed at 0.404 nm), tetracalcium aluminate – 10 hydrate (C_4AH_{10} identified at 0.279 and 0.246 nm) occur in C_3A+H_2O paste in minor amounts

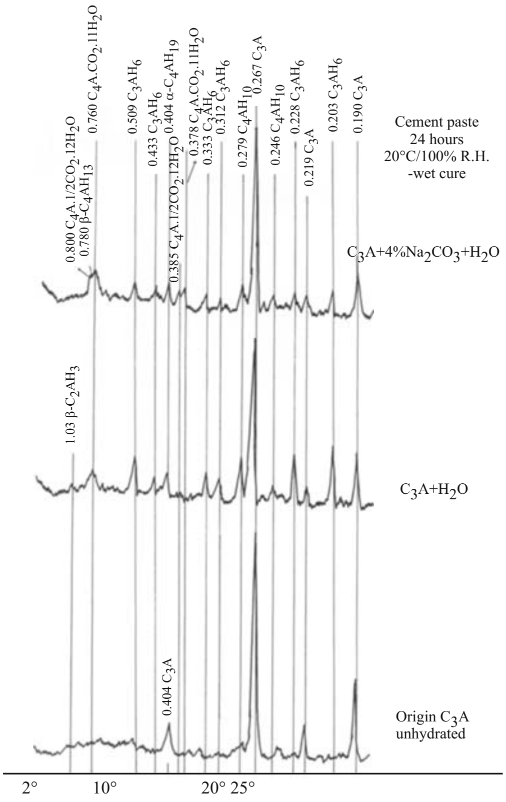

Fig. 8 X-ray diffraction patterns of unhydrated C_3A and C_3A pastes: either the control or with 4 mass% of Na_2CO_3 after 24 h hydration

compared to those of C_3AH_6. As carbonation follows up carbonate aluminate hydrate of type tetracalcium monocarbonate – 11 hydrate ($C_4A{\cdot}CO_2{\cdot}$ $11H_2O$ pattern at 0.760 nm) is present. The comparative analysis of the powder patterns of C_3A+H_2O and $C_3A+4\%$ $Na_2CO_3+H_2O$ pastes shows that both pastes contain similar content of unhydrated C_3A. This indicates the same degree of conversion of tricalcium aluminates to aluminate hydrate phases at 24 h early stage hydration. Patterns of peaks of monocarbonate aluminate hydrate ($C_4A{\cdot}CO_2{\cdot}11H_2O$) become clearer in $C_3A+4\%$ $Na_2CO_3+H_2O$ but the intensity of peaks for C_3AH_6 decreases when compared to C_3A+H_2O paste. Moreover two new peaks appear; that for tetracalcium aluminate – 13 hydrate (β-C_4AH_{13} at 0.780 nm) and tetracalcium aluminate hemicarbonate – 12 hydrate ($C_4A{\cdot}1/2CO_2{\cdot}12H_2O$ at 0.385 nm). For better X-ray examination of hydrated C_3A systems water suspensions were prepared (Fig. 9). The C_3A+H_2O pastes were done with w/c of 0.5 whereas suspensions with w/c ratio of 5.0. The comparative analysis of the powder patterns between C_3A pastes and suspensions shows that there are no detectable changes in the peak positions, although some peaks disappeared and the other become clearer. Reflections of C_3A have almost disappeared in suspensions. There is only a slight diffraction line of unreacted C_3A at 0.190 nm. This evidently confirms the higher degree of hydration in C_3A suspensions relative to that in C_3A pastes. Intensity of diffraction peaks of C_3AH_6 slightly decreases in $C_3A+4\%$ $Na_2CO_3+H_2O$ suspension compared to the control C_3A+H_2O. The analysis indicates evident differences in intensities of many of the reflections between 4 to 6 2Θ and 10 to 12 2Θ, and also occurrence of some new peaks when comparing the XRD results of C_3A+H_2O and $C_3A+4\%$ $Na_2CO_3+H_2O$ suspensions. Between 4 and 6 2Θ, there has been observed a peak at 0.760 nm in C_3A+H_2O suspension, typical for $C_4A{\cdot}CO_2{\cdot}11H_2O$. Moreover in the case of powder analysis of $C_3A+4\%$ $Na_2CO_3+H_2O$, two new peaks are observed at 0.780 nm for α-C_4AH_{13} and at 0.800 nm for $C_4A{\cdot}1/2CO_2{\cdot}12H_2O$. Patterns of peaks at 0.385 nm for $C_4A{\cdot}1/2CO_2{\cdot}12H_2O$ and at 0.378 nm for $C_4A{\cdot}CO_2{\cdot}11H_2O$ become clearer in $C_3A+4\%$ $Na_2CO_3+H_2O$ between 10 and 12 2Θ when compared to relevant reflections in C_3A+H_2O suspension. Moreover new peak at 0.404 nm typical for α-C_4AH_{19} appears.

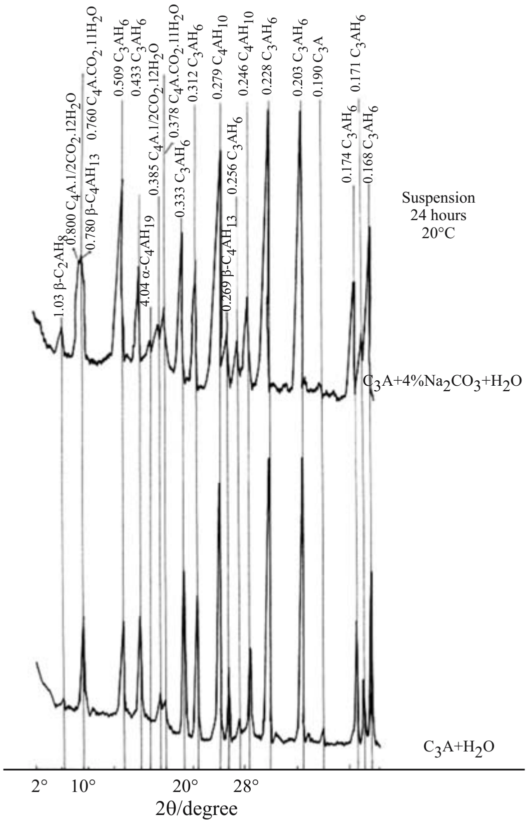

Fig. 9 X-ray diffraction patterns of C_3A water suspensions either the control or with 4 mass% of Na_2CO_3 after 24 h hydration

X-ray examination of the C_3A+H_2O and $C_3A+4\%$ $Na_2CO_3+H_2O$ pastes after 28-day hydration in 20°C/100% R. H. – wet air shows (Fig. 10) that the intensity of peaks for C_3AH_6 at 0.509, 0.433, 0.333, 0.312, 0.228 and 0.203 nm increases relatively to those found in the pastes after 24 h hydration. Intensity of peaks for unreacted C_3A is decreased. It is observed that patterns of peaks typical for α-C_4AH_{19}, C_4AH_{10} and $C_4A{\cdot}CO_2{\cdot}11H_2O$ become clearer in the pastes after longer period of hydration, and contemporarily peak intensities of the above hydration products are getting clearer in $C_3A+4\%$ $Na_2CO_3+H_2O$ paste opposite to those appeared in C_3A+H_2O system.

The results have been interpreted to indicate the occurrence of two distinct stages in the course of hydration reactions of cement pastes with Na_2CO_3 addition. The first concerns the formation of gel-like hydration products of C–S–H and C–A–H types with consequent microcrystalline $Ca(OH)_2$ particle development. High-lime C–S–H products are unstable with respect to its surroundings due to the excess of CO_3^{2-} ions and are quickly transformed to calcite and vaterite in the cement paste. This process lasts very intensively up to 24 h of the hydration, also due to intense calcium aluminate hydrate and calcium carbonate aluminate hydrate formations within the first 24 h. Acceleration of gel-like hydration products development of calcium silicate and calcium aluminate types and formation of larger volume of the hydrate phase in a volume unit of the bulk mass in the cement paste with 2 to 4 mass% of Na_2CO_3 within 24 h result in early strength increases relative to those in the

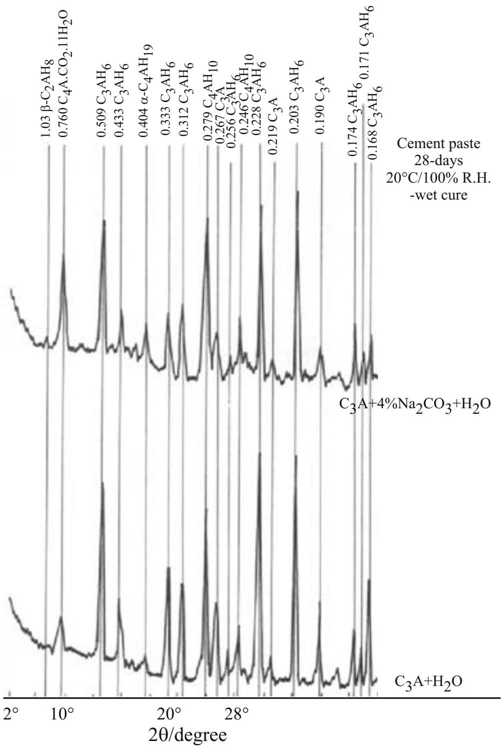

Fig. 10 X-ray diffraction patterns of the control C_3A paste and with 4 mass% of Na_2CO_3 after 28-day hydration at 20°C/100% R. H. – wet air

control paste. The quickly formed hydrate phase is also characterized by higher early total porosity (Table 2).

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 Na_2CO_3 is more intense in comparison with that in the control cement paste in each followed time interval. A dense, well-developed network of $CaCO_3$ crystalline nuclei in Na_2CO_3 modified cement pastes at early stage of hydration are observed. This results a progressive formation of $CaCO_3$ crystals per unit volume of hydrated cement paste, capable of gradual reacting with atmospheric CO_2. The degree of carbonation is higher in Na_2CO_3 modified cement pastes relative to the control one. Higher volume of carbonation products in the cement paste with Na_2CO_3 has also contributed to calcium carbonate aluminate hydrates formation. This result appears after finding that carbonate aluminate hydrates are not found in C_3A+H_2O paste and suspension. A preferential carbonation of the bonding hydrate phase in the Na_2CO_3 modified cement paste and C_3A+H_2O systems is found. The dependence between the cement paste mixture composition and important engineering properties is well recognized [27–30]. With time of hydration compressive strength is markedly increased whereas total porosity is pronouncedly decreased in the control cement paste relative to those found in the pastes with 2 and 4 mass% of Na_2CO_3.

Conclusions

The following conclusions are applicable to the particular test materials and test methods employed:

- The higher Na_2CO_3 percentage, the higher strength growth at total porosities ranging between 50.17 and 51.30% after 24 h hydration at 20°C/100% R. H. wet air is found. The higher Na_2CO_3 percentage, the lower strength growth between 28 and 365 days dry (20/ 60% R. H.) and wet (20°C/100% R. H.) air cure is recognized. The higher Na_2CO_3 percentage, the

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

Type of cement paste	Property of the cement paste at w/c=0.5	Hydration of cement pastes in time					
		6 h	24 h	28 days		365 days	
		W	W	D	W	D	W
Control	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 admixture of 2 mass% of $NaCO_3$	Compressive strength/MPa	0	3.3	9.8	15.5	16.9	23.0
	Specific gravity/g cm^{-3}	2.735	2.732	2.547	2.257	2.708	2.493
	Volume density/g cm^{-3}	1.222	1.343	1.464	1.336	1.571	1.452
	Porosity/% vol.	55.34	50.86	42.79	40.86	41.96	41.75
With admixture of 4 mass% of $NaCO_3$	Compressive strength/MPa	0.2	4.3	11.3	11.6	10.6	17.6
	Specific gravity/g cm^{-3}	2.803	2.704	2.521	2.256	2.605	2.439
	Volume density/g cm^{-3}	1.370	1.316	1.422	1.370	1.457	1.443
	Porosity/% vol.	51.13	51.30	43.60	39.29	44.10	40.86

higher total porosity indicating the coarser pore structure formed in the cement pastes independently on curing regime is observed. Total porosity is by 9.76% lower in the control cement paste after 365 days wet air cure relative to that observed in the paste with 4 mass% of Na_2CO_3.

- The rate of carbonation of Na_2CO_3 modified cement pastes is progressively accelerated in each time interval due to the excess of CO_3^{2-} 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 increased total porosity in Na_2CO_3 modified cement pastes relative to those observed in control specimens, cured 365 days in dry and wet air.

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