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Hydration products of C_3A, C_3S and Portland cement in the presence of $CaCO_3$

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Abstract

The subject of this work is the effect of calcium carbonate on the hydration products of C_3A, C_3S and cement. Pastes made from C_3A and C_3S containing 0%, 10%, 20% and 35% w/w of chemical grade $CaCO_3$, as well as pastes made from Portland cement containing 0%, 10%, 20% and 35% w/w limestone, were examined after 1, 2, 7 and 28 days of hydration. The hydration products in C_3S and C_3A pastes containing $CaCO_3$, as well as in limestone cement pastes, were identified by means of powder diffraction. The effect of calcium carbonate on the hydration procedure was also recorded. It is concluded that in pastes containing $CaCO_3$, either as a chemical reagent or as a limestone constituent, the ettringite's transformation to monosulfate is delayed, while calcium aluminate monocarbonate is preferably formed instead of monosulfate even at early ages. In addition, the hydration of C_3S is accelerated and formation of some carbosilicate is observed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydration products; $Ca_3Al_2O_6$; Ca_3SiO_5; $CaCO_3$; Limestone cement

1. Introduction

The use of blended Portland cements, especially those containing limestone, seems to have many benefits, both technical and economical [1–5]. The European Standard prEN 197-1 identifies two types of Portland limestone cement containing 6–20% limestone (type II/A–L) and 21–35% limestone (type II/B–L), respectively. The limestone must meet three requirements: (a) $CaCO_3$ content greater than 75%; (b) clay content, determined with methylene blue test (MBA), less than 1.20 g/100 g; and (c) total organic carbon (TOC) less than 0.5% [6,7].

The research work in the field of limestone cements is focused on three areas. The first one is the effect of limestone on the cement and concrete performance [4, 5, 8–16]. The competitive behavior of limestone cements is attributed to the filler effect of the fine particles, the increase of the hydration rate, the formation of carboaluminates and the modification of the microstructure. The second one deals with the participation of limestone in the hydration reactions of clinker, while the third one with the production process and specifically the intergrinding of clinker and limestone [8, 17–19]. Although there is a disagreement in many areas, the knowledge level is satisfactory and continuously expanding.

As far as the hydration process is concerned, it is generally accepted that limestone participates in the hydration reactions rather than being an inert filler. Limestone reacts with calcium aluminate to form calcium aluminate carbonates, especially in C_3A-rich cements. The carbonates exist in high and low form with structure and properties presenting analogies with the sulfate equivalents: mono and trisulfoaluminates [20,21]. The most common type of carbonates, found in limestone cement, is the monocarbonate, although some researchers claim that tricarbonate is also formed, in a lesser degree [12,20,22–24]. The mechanism proposed for the carbonate formation is the slow dissolution of calcium carbonate and its reaction with monosulfate or calcium aluminate hydrates to monocarboaluminate, which is more stable because of its greater insolubility [20,22]. There is some disagreement on the estimation of the limestone amount that is incorporated into a cement system, as well as on

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Table 1
Chemical composition of raw mixtures and thermal treatment conditions

	Chemical composition (%)			
Raw mix	CaO	Al_2O_3	SiO_2	MgO
C_3A	62.2	37.8	0.0	0.0
C_3S	71.9	0.6	25.7	1.8
Thermal treatment				
C_3A	800°C, 1 h; 1000°C, 2 h; 1350°C, 19 h;			
C_3S	1600°C, 16 h			

Table 2
Chemical composition of clinker and limestone. Mineralogical composition of clinker

Chemical composition (%)			Mineralogical composition of clinker (%)	
	Clinker	Limestone		
SiO_2	21.79	0.61	C_3S	65.15
Al_2O_3	5.13	0.15	C_2S	13.32
Fe_2O_3	3.59	0.17	C_3A	7.54
CaO	66.42	53.36	C_4AF	10.92
MgO	1.71	1.47	Moduli	
K_2O	0.55	0.02	LSF	95.70
Na_2O	0.09	0.00	SR	2.50
SO_3	0.52		AR	1.43
LOI		43.54	HM	2.18

the effect of calcium carbonate on the transformation of ettringite to monosulfate. Both prevention and acceleration of this reaction have been reported [20,23,25]. The incorporation of limestone in calcium silicate hydrates and the acceleration of C_3S hydration have also been proposed [25–27]. The maximum quantity of $CaCO_3$ that can react appears to be 2–3% with most cements, but values up to 5.8% have been claimed [24].

The present work deals with the effect of calcium carbonate, first, on the hydration of individual components of clinker and then on the hydration of cement. More specifically, C_3A and C_3S containing 0–35% w/w calcium carbonate and Portland cement containing 0–35% w/w limestone are hydrated for 1–28 days and are examined by means of X-ray diffraction in order to identify the hydration products. This work is a part of a project, developed in our laboratory, concerning the properties of limestone cement and concrete.

2. Experimental

Laboratory synthesized C_3S and C_3A were used in order to prepare mixtures with 0%, 10%, 20%, and 35% w/w $CaCO_3$. In addition, limestone cements containing 0%, 10%, 20%, and 35% w/w limestone were examined. Chemical grade $CaCO_3$ is added in C_3S and C_3A, while mineral limestone is added in the cement, in order to study the hydration process in the system of pure compounds and the real system of industrial limestone cement.

Table 1 presents the chemical composition of the mixtures used for the preparation of C_3A and C_3S, as well as the conditions of their thermal treatment. Al and Mg oxides are added in the C_3S raw mix in order to have a product similar to alite found in clinker. Besides, these compounds promote the formation of C_3S at lower temperature. After the thermal treatment, the samples were ground to size less than 90 μm and mixed with 0%, 10%, 20%, and 35% $CaCO_3$. In the case of C_3A, 20% gypsum w/w (on C_3A basis) is also added. The samples are referred as C_3A-i and C_3S-i, i being the $CaCO_3$ content.

Limestone Portland cement are produced by intergrinding of industrial clinker, gypsum and limestone. Four samples having limestone content 0%, 10%, 20%, and 35% are studied. The samples are referred as LC-0, LC-10, LC-20, and LC-35, respectively. The chemical and mineralogical composition (Bogue) of the used clinker, as well as the chemical composition of limestone are shown in Table 2. The main constituent of the limestone is calcite containing also dolomite and quartz as minor constituents. The specific surface, according to Blaine apparatus, the % residue at 32 μm, the compressive strength after 1, 2, 7 and 28 days, the standard consistency and the setting time of the produced cements are given in Table 3.

Pastes were prepared by mixing solid and carbon dioxide-free distilled water in polyethylene vials sub-

Table 3
Properties of limestone cements

	Fineness								
		Specific surface	Compressive strength (N/mm^2)				Standard consistency	Setting time (min)	
Sample	R_{32} (%)	(cm^2/g)	1 Day	2 Days	7 Days	28 Days	(%)	Initial	Final
LC-0	25.3	3110	12.6	23.9	40.6	52.9	25.7	140	190
LC-10	22.3	3830	15.0	25.9	44.0	53.3	25.0	145	195
LC-20	24.5	4330	11.0	21.4	37.6	45.9	23.2	110	180
LC-35	22.6	5150	7.5	15.9	27.2	33.5	22.8	100	165

Table 4
Hydration products in pastes C_3A-0 and C_3A-35

Hydration products	1 Day		2 Days		7 Days		28 Days	
	C_3A-0	C_3A-35	C_3A-0	C_3A-35	C_3A-0	C_3A-35	C_3A-0	C_3A-35
Ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 25H_2O)$	✓	✓	✓	little	little			
Calcium aluminum oxide sulfate hydrate $(Ca_3Al_2O_6\cdot CaSO_4\cdot 13H_2O)$	✓		✓	✓	✓	✓	✓	✓
Calcium aluminum sulfate hydrate $(Ca_3Al_2O_6\cdot CaSO_4\cdot 14H_2O)$				✓		✓		✓
Calcium aluminum oxide carbonate hydrate $(Ca_4Al_2O_6\cdot CO_3\cdot 11H_2O)$		✓		✓		✓		✓
Calcium aluminum oxide carbonate hydroxide hydrate $(Ca_4Al_2O_6\cdot (CO_3)_{0.5}(OH)\cdot 11.5H_2O)$				✓		✓		
Calcium aluminum oxide hydrate $(CaAl_2O_4\cdot 10H_2O)$						✓		✓
Calcium aluminum oxide hydroxide hydrate $(3CaO\cdot Al_2O_3\cdot Ca(OH)_2\cdot 18H_2O)$			✓	✓	✓	✓	✓	✓
Calcium aluminum oxide hydroxide hydrate $(Ca_6Al_2O_6(OH)_6\cdot 32H_2O)$					✓		✓	
Calcium aluminum oxide hydrate $(Ca_2Al_2O_5\cdot 8H_2O)$				✓		✓	✓	✓

jected to rotation from time to time. The water to solid ratio used for C_3A system is 0.8, whereas that for C_3S and cement is 0.3. After a period of 1, 2, 7 and 28 days, the samples were dried in vacuum for 24 h and subjected to X-ray diffraction.

Thermogravimetric analysis (TGA) was used for the determination of non-evaporable water and calcium hydroxide content in dried cement pastes, using a TA Instruments Thermal Analyst 3000. The samples ($\sim$ 50 mg) were heated over the range 20°C to 900°C at a constant rate of 15°C/min in an atmosphere of carbon dioxide-free nitrogen, flowing in 90 cm^3/min.

3. Results and discussion

The hydration products of Portland cement do not have very clear diffraction peaks, due mainly to their semi-amorphous nature. Besides, there is overlapping of peaks of the hydrated and anhydrous compounds. In order to identify the hydration products from the XRD patterns of the pastes, the following steps were made:

- The samples were carefully ground to size less than 54 μm.
- The patterns of the anhydrous compounds and the limestone were taken in consideration in order to exclude their peaks from the patterns of the pastes.
- In the region $2\theta = 5-15°$, the count time was increased in order to record clearly the small peaks of ettringite, C-S-H and carboaluminates.
- The evaluation of the data was made individually for each sample, as well as comparatively for samples having the same limestone content at different ages and for samples having different content at the same age.

3.1. Hydration products in C_3A and C_3A+$CaCO_3$ pastes

The products identified by XRD in C_3A-0 and C_3A-35 pastes are presented in Table 4. Fig. 1 indicatively shows the XRD patterns of these samples after 28 days of hydration. The main differences among pure

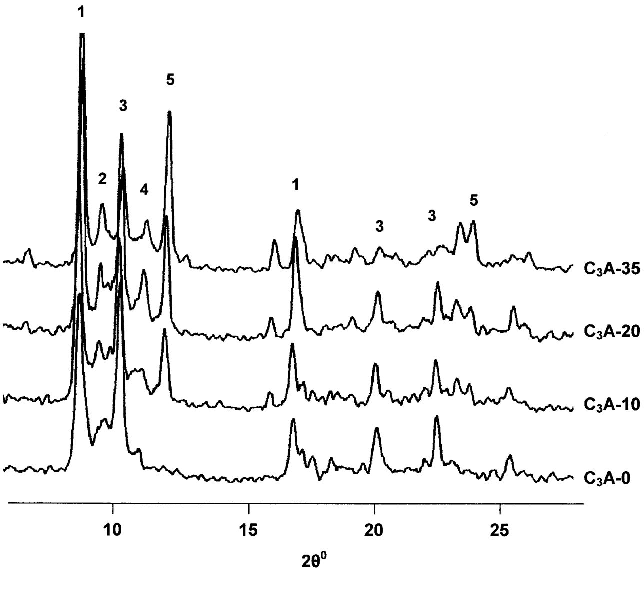

Fig. 1. XRD patterns of C_3A-0, C_3A-10, C_3A-20 and C_3A-35 pastes after 28 days. (1) $3CaO\cdot Al_2O_3\cdot Ca(OH)_2\cdot 18H_2O$, (2) $Ca_3Al_2O_6\cdot CaSO_4\cdot 14H_2O$, (3) $Ca_3Al_2O_6\cdot CaSO_4\cdot 13H_2O$, (4) $Ca_4Al_2O_6\cdot CO_3\cdot 11H_2O$, (5) $Ca_4Al_2O_6\cdot (CO_3)_{0.5}(OH)\cdot 11.5H_2O$.

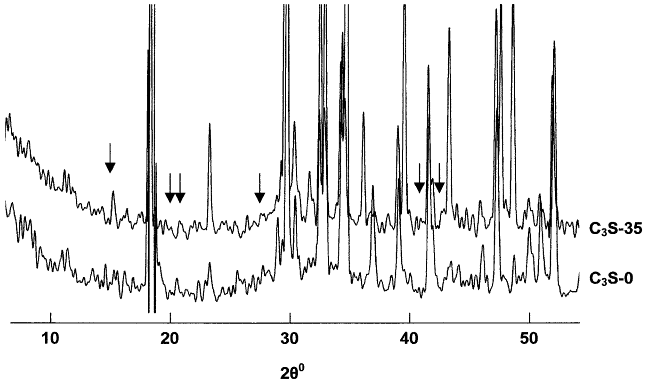

Fig. 2. XRD patterns of C_3S-0 and C_3S-35 pastes after 28 days (arrows indicate the peaks attributed with the carbosilicate hydrate).

pastes and pastes with calcium carbonate concern the transformation of ettringite to monosulfate and the formation of carboaluminates.

Ettringite is formed during the first 24 h in all samples. Small quantity of ettringite is probably present up to 7 days, in all samples, but it disappears at 28 days. Pastes with calcium carbonate appear to contain lesser ettringite than in plain cement pastes, even if the dilution of the samples with limestone is taken into account. Monosulfate has already formed in pure cement pastes during the first 24 h and continues to be formed up to 28 days. In pastes with calcium carbonate, monosulfate is formed after 2 days and is still present at 28 days in continually decreased amount.

In pastes with $CaCO_3$, monocarbonate hydrate ($Ca_4Al_2O_6 \cdot CO_3 \cdot 11H_2O$) is formed from the beginning even in sample C_3A-10, and continues to increase up to 28 days. At 2 and 7 days, another form of carboaluminate ($Ca_4Al_2O_6 \cdot (CO_3)_{0.5}(OH) \cdot 11.5H_2O$) with increased CaO/$CO_3^{-2}$ ratio is detected.

Based on the above observations, it is concluded that calcium carbonate suppresses the conversion of ettringite to monosulfate and favors the replacement of monosulfate by monocarbonate. This may be due to the greater insolubility and therefore the greater stability of carbonate.

The addition of calcium carbonate does not cause great changes as far as the type of calcium aluminate hydrates is concerned, but it affects their rate of formation. $3CaOAl_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$ and $Ca_2Al_2O_5 \cdot 8H_2O$ are detected in all samples, the former being formed earlier in pure cement pastes while the latter in pastes containing calcium carbonate. In pure pastes, $Ca_6Al_2O_6(OH)_6 \cdot 32H_2O$ is formed after 7 days. It must be noticed, however, that it is difficult to distinguish the different forms of C_3A hydrates since many of them have similar diffraction patterns.

3.2. Hydration products in C_3S and C_3S+$CaCO_3$ pastes

The hydration products of C_3S are not clearly observed, due to their semi-amorphous nature. Comparing the patterns of each sample at different ages, it is concluded that the band at $2\theta = 25-35°$, which is characteristic of calcium silicate hydrates, progressively increases, while the C_3S peaks decrease. CH peaks also increase in relation to hydration time. However, XRD quantitative determination of CH cannot be done, since part of it may not be well crystallized. There are indications, that small amounts of a type of carbosilicate hydrate (probably scawtite, $Ca_7(Si_6O_{18})(CO_3) \cdot 2H_2O$) are formed in samples containing $CaCO_3$. Fig. 2 presents the XRD patterns of the C_3S-0 and C_3S-35 samples after 28 days of hydration.

3.3. Hydration products in limestone cement pastes

Table 5 shows the hydration products in the pure cement paste (LC-0) and cement paste containing 35% limestone (LC-35). In LC-0 pastes, ettringite is gradually transformed into monosulfate. In LC-35 pastes, the formation of ettringite is delayed and monocarboaluminate is preferably formed instead of monosulfate. Calcium aluminate hydrates ($3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$

Table 5
Hydration products in samples LC-0 and LC-35

	1 Day		2 Days		7 Days		28 Days	
Hydration products	LC-0	LC-35	LC-0	LC-35	LC-0	LC-35	LC-0	LC-35
Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$)	✓	little	✓	✓	✓	✓	✓	✓
Calcium aluminum oxide sulfate hydrate ($Ca_3Al_2O_6 \cdot CaSO_4 \cdot 13H_2O$)	little		✓	✓	✓	✓	✓	✓
Calcium aluminum oxide carbonate hydrate ($Ca_4Al_2O_6 \cdot CO_3 \cdot 11H_2O$)				✓		✓		✓
Calcium aluminum oxide hydroxide hydrate ($3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$)					✓		✓	
Calcium aluminum oxide hydroxide hydrate ($Ca_6Al_2O_6(OH)_6 \cdot 32H_2O$)					✓		✓	
Calcium aluminum oxide hydrate ($Ca_2Al_2O_5 \cdot 8H_2O$)							✓	

Table 6
Non-evaporable water and CH content in limestone cement pastes

	Non-evaporable water (%)			$Ca(OH)_2$ (%)		
Sample	2 Days	7 Days	28 Days	2 Days	7 Days	28 Days
LC-0	18.72	23.72	24.44	9.43	14.55	16.05
LC-10	21.75	24.46	24.78	9.10	20.59	19.80
LC-20	20.22	26.62	27.75	8.95	18.52	18.35
LC-35	19.01	28.65	29.36	9.98	16.03	16.13

and $Ca_2Al_2O_5{\cdot}8H_2O$) are detected in LC-0 pastes, but not in limestone pastes, probably because of the dilution of the samples by limestone.

The CH and non-evaporable water determined by TGA are shown in Table 6. Both CH and non-evaporable water are expressed as a percentage of weight of clinker + gypsum rather than clinker + gypsum + limestone (cement) since this enables the effect of limestone addition on hydration to be illustrated more clearly. The higher content of bound water in the pastes made from limestone cements, indicates that limestone improves the clinker reactivity and exploits its hydraulic potential. This effect may be related to the structure modification of the hydration. The increase of CH content in pastes of limestone cement indicates an acceleration of calcium silicate hydration.

4. Conclusions

The hydration products in C_3S and C_3A pastes containing $CaCO_3$, as well as in limestone cement pastes, are identified by means of powder diffraction. The effect of calcium carbonate on the hydration procedure is also recorded. It is concluded that, in pastes containing $CaCO_3$, either as a chemical reagent or as a limestone constituent, the ettringite's transformation to monosulfate is delayed, while calcium aluminate monocarbonate is preferably formed instead of monosulfate even at early ages. In addition, the hydration of calcium silicates is accelerated.

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