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The influence of the alite polymorphism on the strength of the Portland cement

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Abstract

The influence of the alite polymorphism on the strength of cement was monitored in a set of laboratory-prepared clinkers with equal quantitative phase composition and different ratio of modifications. The alite polymorphism in clinkers was influenced by the change of the MgO and SO_3 side oxides in clinker, raw meal reactivity change, raw meal preheating, burning temperature or by the adding of crystallisation nuclei. The differences in the hydraulic properties of the M_1 and M_3 modifications were determined. In the case of all the hydration periods monitored, the strength of cements with the M_1 modification was 10% higher than the strength of cements with the M_3 modification. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Alite is the principal hydraulic phase of clinker, having the decisive impact on the strength of Portland cement. Alite is a solid solution of Ca_3SiO_5 with minor oxides.

Ca_3SiO_5 is characterised by an extensive polymorphism. Seven structural modifications have been identified [1,2] with enantiomorphic transformations—three triclinic (T), three monoclinic (M) and one trigonal—the transformation temperatures of which (°C) can be observed in the following scheme:

$$T_1 \xleftrightarrow{620} T_2 \xleftrightarrow{920} T_3 \xleftrightarrow{980} M_1 \xleftrightarrow{990} M_2 \xleftrightarrow{1060} M_3 \xleftrightarrow{1070} R.$$

In clinker, alite always crystallises from the melt in a trigonal form. The stabilisation factors decide during the cooling process which modification stable at ambient temperature is formed. For this reason, alite forms morphologically trigonal pseudomorphs in clinker. The most common modifications are M_1 and M_3, and T_2 occurs only rarely [3]. The ratio of the nucleation processes and alite crystallisation, and the contents of minor oxides in the melt are the decisive stabilisation factors. High intensity of nucleation and slow, stable crystal growth together with increased MgO stabilise M_3. On the contrary, high growth rate and non-stable crystal growth at low nucleation and increased SO_3 lead to M_1 stabilisation [4–6]. At high melt oversaturation, the slow steady crystallisation during an intense nucleation results in the growth of smaller idiomorphic crystals of M_3 with a low number of inclusions. In the case of a low oversaturation of the melt, crystal growth predominates over nucleation; low number of nuclei leads to fast growth of large irregularly shaped M_1 crystals with abundant inclusions of belite and interstitial matter.

These genetic markers help to identify alite microscopically in clinker. The distinguishing features are different birefringence and type of twinning. The M_3 form has two times higher birefringence than M_1; T_2 is characterised by the lowest birefringence and inverse polysynthetic twinning. The polymorphs can also be identified by X-ray diffraction [7,8]. Alite modifications can also be reliably identified by high-temperature microphotometry, giving the variation of birefringence as a function of temperature [2,9,10].

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Only little attention has been paid to the influence of the polymorphism on the process of hydration. In some works dealing with the influence of the polymorphism of Ca_3SiO_5 [11–13], the influence of the alite modifications on the strength of cement was not researched at all.

It is well known that the strengths of cements from different localities differ a lot in spite of a high similarity of the contents of alite and other phases. Almost always, such differences are looked upon as results of different concentrations of the minor oxides, especially SO_3, alkali oxides and MgO. The low content of these oxides has a significant influence on the polymorphism of clinker phases, and particularly on alite, the principal hydraulic phase. This study focuses on the verification of this hypothesis.

2. Experimental

Twenty-one clinkers containing different alite modifications were prepared in the laboratory. Cements from these clinkers were ground to the same specific surface.

2.1. Preparation of raw meals and burning of clinker

Cement raw meals, natural limestone, silica sand and chemical compounds Fe_2O_3, $Al(OH)_3$, $MgCO_3$, $CaSO_4 \cdot 2H_2O$, K_2CO_3 and Na_2CO_3 were used as raw materials. The experimental sampling was based on three raw meals, resulting in M_1 alite modification (named mM1), M_3 alite modification (named mM3) and a mixture of modifications M_1 and M_3 (named m(M1M3)). The occurrence of individual alite modifications in clinkers was controlled by:

- the change of the contents of the MgO and SO_3;
- the change of the raw meal reactivity;
- the preheating of the raw meal, by the temperature of burning or by addition of crystallisation nuclei.

In order to maintain a similar quantitative phase composition, it was necessary to burn the individual clinkers until a constant content of free CaO in the clinker (1 wt.%). The time of isothermal burning had to be determined in advance so that this grade could be reached. For this purpose, the kinetic Eq. (1) was applied of the formation of alite in the process of isothermal burning [14]. The phase composition was determined microscopically by point counting [15]; all 21 clinkers had approximately the same phase composition, given in Table 1. The alite polymorphs were identified by high-temperature microphotometry [9] and X-ray powder diffraction [7].

Table 1
Average phase composition of clinkers in weight percent

	Phase				
	C_3S	C_2S	C_3A	C_4AF	Free CaO
Content	64	14	11	10	1

Table 2
Clinkers in which the alite modification was influenced by MgO and SO_3 contents

Original raw meal	Mode of influencing	MgO content in clinker	SO_3 content in clinker	Modification of alite	Name of clinker
mM3	–	0.90	0.04	M_3	sM3
	Increase of SO_3 content	0.89	0.77	M_3+M_1	sM3/1S
	Increase of SO_3 content	0.77	1.73	M_1	sM3/3S
m(M1M3)	Increase of MgO content	1.89	1.30	M_3	s(M1M3)/1M
	–	0.89	1.45	M_1+M_3	s(M1M3)
	Increase of SO_3 content	0.85	2.31	M_1	s(M1M3)/2S
mM1	–	1.07	1.26	M_1	sM1
	Increase of MgO content	1.36	1.29	M_1+M_3	sM1/0.25M
	Increase of MgO content	2.11	1.28	M_3	sM1/1M

$$F(\alpha_A) = (1 - \sqrt[3]{1 - \alpha_A})^2 \tag{1}$$

where α_A = conversion step of $C + C_2S = C_3S$ reaction determined upon alite contents and free lime in clinker.

2.2. Preparation of cements and determination of the strength

Cements were prepared from clinkers ground at equal specific surface ($310 \pm 5\ m^2\ kg^{-1}$). The setting was con-

Table 3
Clinkers in which the alite modification was influenced by the change of the raw meal reactivity

Original raw meal	Mode of influence	Granulometry	Modification of alite	Name of clinker
mM3	–	Original	M_3	sM3
	Decrease in reactivity	20% fraction (0.1–0.2 mm)	M_3+M_1	sM3/H1
	Decrease in reactivity	40% fraction (0.1–0.2 mm)	$M_1>M_3$	sM3/H2
m(M1M3)	Increase in reactivity	Below 0.063 mm	M_1+M_3	s(M1M3)/63
	–	Original	M_1+M_3	s(M1M3)
	Decrease in reactivity	20% fraction (0.1–0.2 mm)	M_1	s(M1M3)/H
mM1	–	Original	M_1	sM1
	Increase in reactivity	Below 0.090 mm	$M_1>M_3$	sM1/90
	Increase in reactivity	Below 0.063 mm	$M_1>M_3$	sM1/63

Table 4
Clinkers in which the alite modification was influenced by the preheating of the raw meal, burning temperature and addition of crystallisation nuclei

Original raw meal	Mode of influence	Actual conditions	Modification of alite	Name of clinker
mM3	–	–	M_3	sM3
	Preheating	60 min at 1100 °C	$M_1 > M_3$	sM3/P
	Preheating + slow cooling process	60 min at 1100 °C, slow cooling process from 750 °C	M_1	sM3/P/750
m(M1M3)	Preheating	60 min at 1100 °C	M_1	s(M1M3)/P
	–	–	$M_1 + M_3$	s(M1M3)
	Increase of burning intensity + nuclei	Burning temperature 1500 °C + 10% nuclei M3	$M_3 > M_1$	s(M1M3)/Z/1500
mM1	–	–	M_1	sM1
	Increase of burning intensity	Burning temperature 1500 °C	$M_1 > M_3$	sM1/1500
	Increase of burning intensity + nuclei	Burning temperature 1500 °C + 10% nuclei M3	$M_1 + M_3$	sM1/Z/1500

trolled by addition of $CaSO_4 \cdot 2H_2O$ corresponding to 3 wt.% in cement. Compressive strength tests were carried out after 2, 7 and 28 days of hydration on 20 × 20 × 100 mm. The cement pastes were prepared featuring an equal cement/water ratio ($w = 0.26$). First, for 24 h, the moulded cement pastes were kept at 20 ± 2 °C and relative humidity exceeding 90%. Then, the beams of mature cement paste were stored in a water storage facility at 20 ± 1 °C. Each resultant value of the compressive strength is an average calculated from six determinations.

3. Results and discussion

3.1. Stability of alite modifications

The conditions of the preparation and composition of alite modifications in clinkers are given in Tables 2–4.

The obtained results imply that the content of MgO and SO_3 in clinker have the greatest influence on the M1 and M3 modification stability. The other factors monitored do not assert such a substantial influence. Besides that, their influence depends to a high degree on the initial properties of the raw meal, i.e. on its chemical composition, grain size distribution, mineral composition, contents of minor oxides (especially MgO and SO_3) and homogeneity (at macro- and microlevel). Other factors that can influence the alite modification are related to the process of burning and cooling of clinker. Such factors are especially the volatilisation of volatile components (SO_3 and alkali); duration time and temperature conditions at calcination; intensity and grade of burning and conditions of cooling.

The preheating of the raw meal at a temperature from 1.100 to 1.200 °C results in the recrystallisation of free CaO. Therefore, during the following burning the solubility of

Table 5
Characteristics of cements — specific surface according to Blaine ($m^2\ kg^{-1}$), contents of SO_3 and K_2O in clinkers (wt.%), SG sulphate module (%), compressive strength (MPa) and alite modifications

Name of cement	Specific surface	Content			SG	Compressive strength			Modification of alite
		SO_3	MgO	K_2O		2 days	7 days	28 days	
cM3	308.2	0.04	0.90	0.39	7	51.7	102.2	122.5	M_3
cM3/1S	309.7	0.77	0.89	0.41	127	68.9	98.2	116.7	$M_3 + M_1$
cM3/3S	311.3	1.73	0.77	0.52	252	79.1	94.9	115.4	M_1
cM3/H1	305.8	0.03	0.59	0.12	11	58.1	105.4	127.4	$M_3 + M_1$
cM3/H2	309.6	0.02	0.46	0.07	11	65.9	110.5	139.6	$M_1 > M_3$
cM3/P	308.0	0.06	0.87	0.24	13	61.5	109.5	130.9	$M_1 > M_3$
cM3/P/750	307.4	0.06	0.87	0.24	13	64.1	113.0	133.6	M_1
c(M1M3)	306.4	1.45	0.89	0.93	132	69.5	91.1	104.5	$M_1 + M_3$
c(M1M3)/1M	311.3	1.30	1.89	0.83	133	70.8	94.5	105.7	M_3
c(M1M3)/2S	307.2	2.31	0.85	1.07	191	66.7	87.4	99.0	M_1
c(M1M3)/63	306.4	1.83	0.88	1.28	131	60.7	78.3	97.1	$M_1 + M_3$
c(M1M3)/H	307.5	0.11	0.53	0.02	91	53.5	103.0	129.7	M_1
c(M1M3)/P	312.4	1.27	0.86	0.81	132	77.7	93.6	105.7	M_1
c(M1M3)/Z/1500	311.1	1.39	1.09	1.01	120	64.8	85.8	99.0	$M_3 > M_1$
cM1	306.8	1.26	1.07	0.75	123	66.2	92.1	112.9	M_1
cM1/0.25M	308.2	1.29	1.36	0.79	122	63.1	90.5	106.1	$M_1 + M_3$
cM1/1M	314.2	1.28	2.11	0.79	121	59.5	79.3	99.9	M_3
cM1/90	305.3	1.65	1.04	0.96	136	58.3	81.0	105.9	$M_1 > M_3$
cM1/63	308.0	1.78	1.05	0.99	142	61.5	75.8	103.3	$M_1 > M_3$
cM1/1500	312.4	1.32	1.07	0.81	120	76.9	91.8	114.1	$M_1 > M_3$
cM1/Z/1500	307.0	1.37	1.25	0.80	133	73.5	91.4	117.1	$M_1 + M_3$

CaO decreases as well as the nucleation of alite [15]. This results in a partial formation of M_1 instead of M_3 formed by usual burning (see Table 4).

The increase in burning temperature results in the increase in the solubility of free CaO and alite nucleation [16]. This should change the conditions in such a way that besides the M_1 modification, the M_3 modification should also be formed. This presumption was confirmed and a clinker with a certain content of M_3 ($\leq 25\%$) besides M_1 was formed from the mM1 meal. However, in this case the contents of SO_3 in clinker played an important role as a M_1 stabiliser. When M_3 crystallisation nuclei are added, the contents of M_3 in clinker increased. However, the dominant influence of SO_3 upon the M_1 modification was retained.

The decrease in the reactivity when a coarser raw meal is added should favour the formation of the M_1 alite modification; the increase in the reactivity due to smaller grain size of the raw meal should favour the formation of the M_3 modification. Table 3 shows that this presumption has been confirmed in the case of the raw meals with lowered

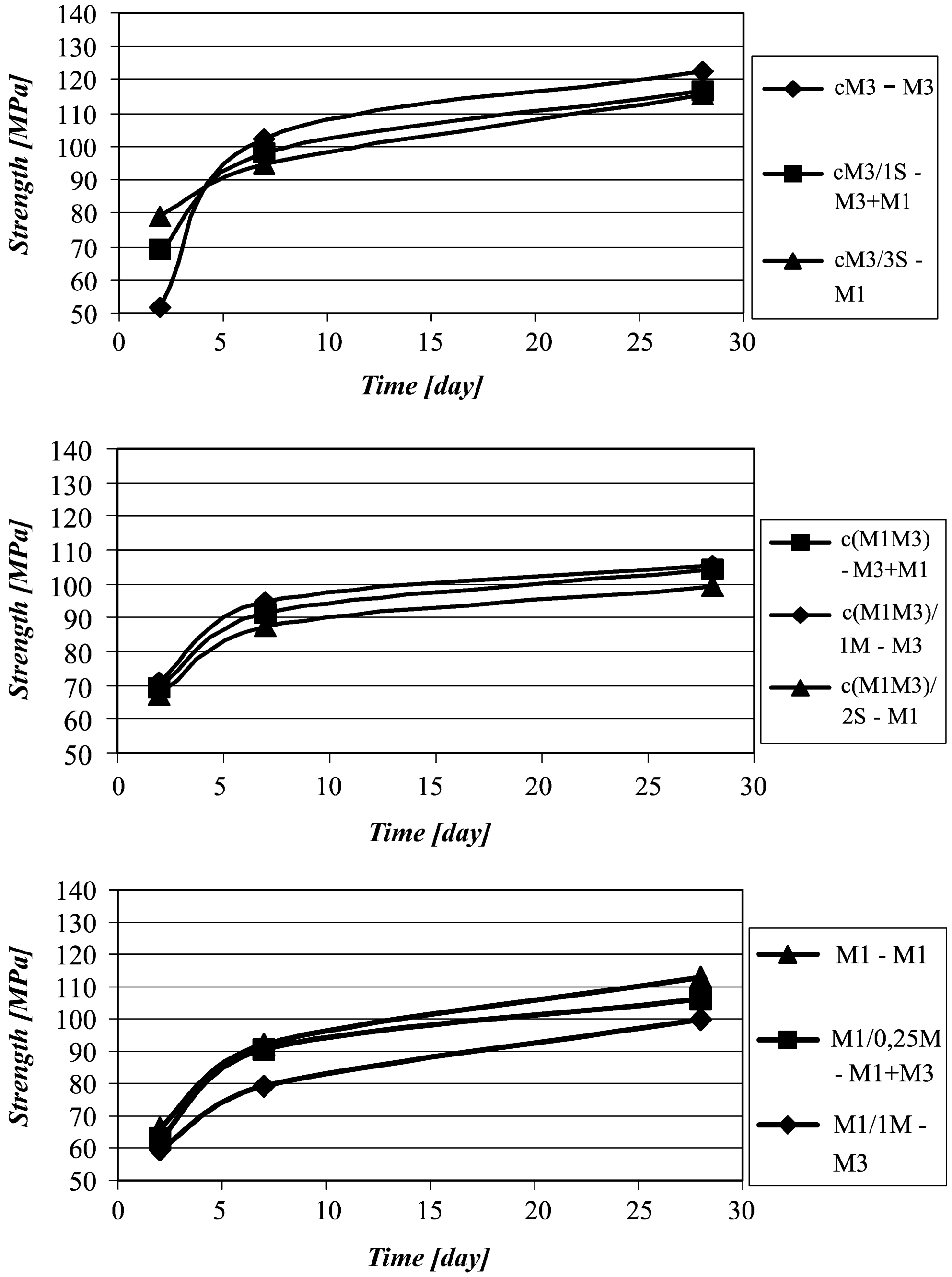

Fig. 1. Compressive strength of cements with alite contents influenced by variable MgO and SO_3 contents in the clinker (description: cement type—modification of alite in the clinker).

reactivity. In the case of the raw meals of higher reactivity, a small content of the M_3 was formed besides the prevailing M_1. The content of SO_3 played an important role, being increased when the burning time of the most reactive raw meals was reduced in comparison with the original mM1 raw meal.

3.2. Influence of alite polymorphism on cement strength

The selected parameters of the individual cements and their resulting strengths are given in Table 5. The development of strengths is shown in Figs. 1–3.

The results indicate that for a given amount of SO_3 in clinker and at all hydration terms, clinkers containing M_1 feature higher compression strengths than those containing M_3. This result was also confirmed in the case of the industrial clinker, in which just the transformation of the original M_3 modification to M_1 occurred without any further changes of composition (Table 6). The transformation was carried out by means of a short heating of the clinker to 800 °C followed by a slow cooling process.

When the M_3 modification changed to M_1 by increasing the contents of SO_3 in clinker, the content of SO_3 and SO_3/alkali ratio in the clinker asserted the dominant

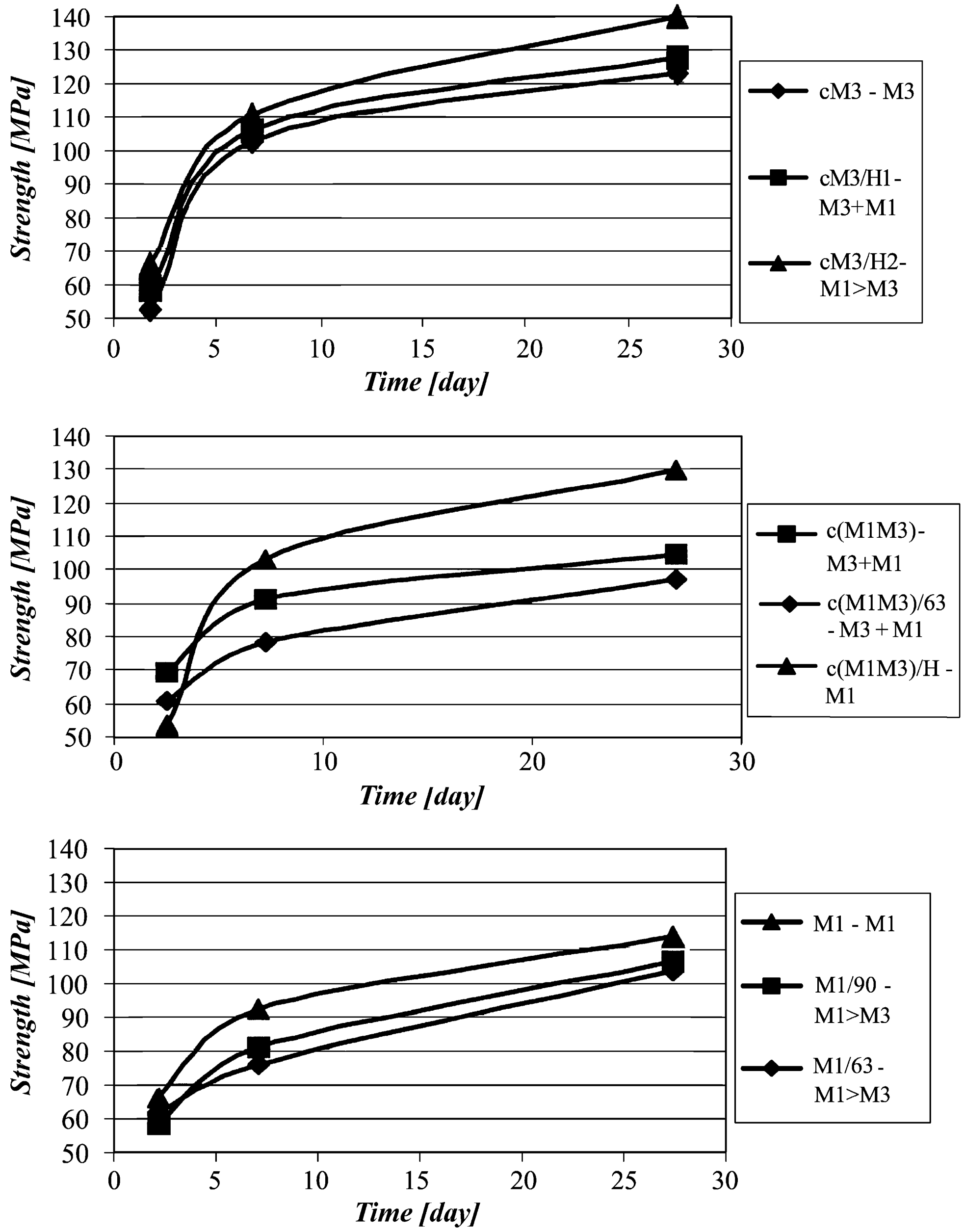

Fig. 2. Compressive strength of cements with alite contents of which was influenced by the change of the reactivity of the source raw meals (description: cement type—modification of alite in the clinker).

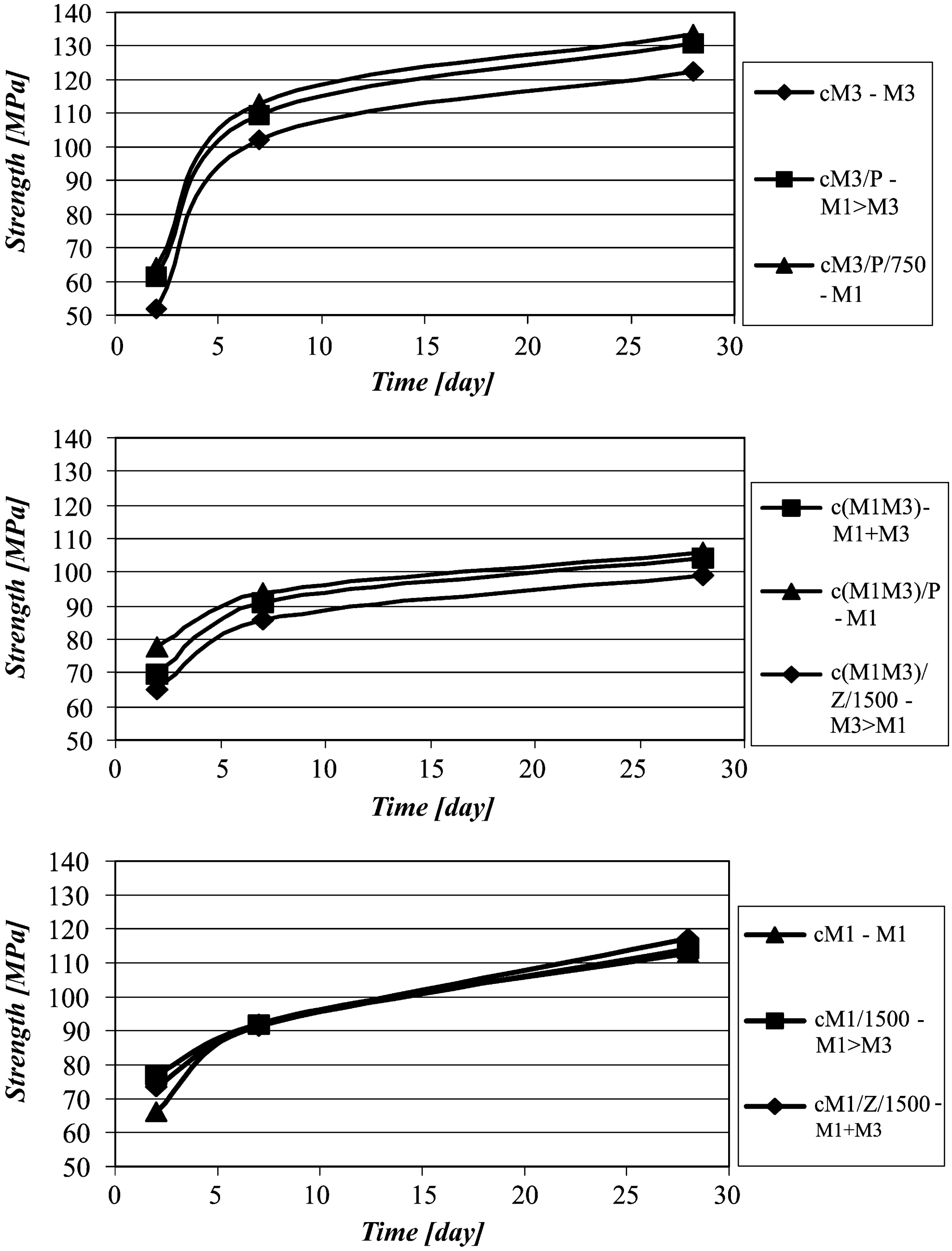

Fig. 3. Compressive strength of cements in which the modification composition of alite was influenced by means of the raw meal preheating, intensification of the burning or crystallisation nuclei addition (description: cement type—modification of alite in the clinker).

influence upon the strength, just as it has been described in literature [17–19]. The influence related to the change of the alite modification will not be reflected in the strength. The increase in SO_3 content increases the short-term strength (after 2 days) and decreases the strength after 7 and 28 days.

Table 6
Characteristics of cements prepared from an industrial clinker-specific surface according to Blaine ($m^2\ kg^{-1}$); contents of SO_3, MgO and K_2O in clinkers (wt.%); SG sulphate module (%); compressive strength (MPa) and alite modifications

		Content				Compressive Strength			
Name of cement	Specific surface	SO_3	MgO	K_2O	SG	2 days	7 days	28 days	Modification of alite
cM	313.6	0.56	0.89	0.97	60	63.6	75.4	97.7	M_3
cM/800	305.2	0.56	0.89	0.97	60	71.0	88.1	107.1	M_1

The change of M_1 into M_3 by increasing the MgO content when the contents of SO_3 is constant results in a decrease in the strength at all hydration terms monitored.

The increase in the M_1/M_3 ratio by decreasing the reactivity results in the strength increase. The only exception is a low 2-day strength of the M1M3/H cement caused by a marked alite recrystallisation in a clinker burned for an extremely long time from a raw meal of extremely low reactivity.

The $M_3 \rightarrow M_1$ transformation due to the preheating of the raw meal also results in the cement strength increase.

The increased reactivity and burning intensification did not lead to the decrease in compressive strength, corresponding to expected increase in the M_3/M_1 ratio. In reality, the M_3/M_1 ratio did not increase, as M_1 was markedly stabilised by the presence SO_3 in clinker, and the contents of the M_3 modification was therefore low. The intensification of the burning and increase in the reactivity provoked a quicker growth of minute, often zoned alite crystals (in this case both M_3 and M_1), thus, increasing partly their hydraulic activity as compared to the sM_1 clinker.

4. Conclusions

The increase of the MgO/SO_3 ratio results in the stabilisation of M_3 polymorph, while decrease of this ratio stabilizes M_1. The preheating of the raw meal may result in the disappearance of the M_3 modification. The other methods of influence applied (the change of the raw meal reactivity; intensification of burning and addition of crystallisation nuclei) do not have comparably strong influence and result only in minor changes in the ratio of both alite forms. The decrease in raw meal reactivity led to partial increase of the M_1/M_3 ratio. The increase of raw meal reactivity; intensification of burning and addition of crystallisation M_3 nuclei resulted in partial decrease of the M_1/M_3 ratio.

It was proved that the M_1 and M_3 monoclinic alite modifications differ in their respective hydraulic characteristics. The transformation of M_3 to M_1 modification may result in a 10% increase in the compressive strength after 2, 7 and 28 days of hydration. Such an increase can be considered significant, as the precision of the compressive strength measurement is ±2%. The reasons of this phenomenon, which should be searched for in the microstructure of alite crystals, will be the subject to further research.

The transformation of M_3 to M_1 by means of an additional heating of clinker to 800 °C followed by a slow cooling could be important for the practical application. Another beneficial application of the research results in cement industry could be the decreasing of MgO as stabilizer of M_3 in clinker at possible simultaneous correction of SO_3 content.

The other methods (preheating and decrease in the raw meal reactivity) result in a higher consumption of energy required for the burning of clinker. If the reactivity decreases due to the lowering of the raw meal fineness, the increase in the consumption of energy required for the burning of clinker would be compensated by a lower consumption of energy required for the raw material grinding and a higher strength of the final product.

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