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SETTING TIME REGULATION OF POLYMER MODIFIED CALCIUM ALUMINATE CEMENT BASED MATERIALS

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Abstract

In comparison to portland cement, calcium aluminate cements (CAC) show relatively slow setting but rapid hardening characteristics. Styrene-butadiene-rubber 1 (SBR) modified cement based materials have been widely used for floor and bridge overlays. A small amount of different organic and inorganic compounds show pronounced influence on setting time of CAC based materials.

In this paper the influence of styrene-butadiene-rubber (SBR) on iron-rich calcium aluminate cement (CAC) hydration was investigated. Cement pastes and mortars with quartz sand (0.5-1mm) and natural sand (0-4mm) with different polymer content (p/c = 0 to 20 %) were prepared. As a set regulator an accelerator Li_2CO_3 was used. Times of initial and final sets were established from measurements of temperature rise of prepared materials. Cement paste series showed high retardation of setting time with SBR addition. Mortar series showed that larger SBR additions ($p/c \geq 6\%$) retard the setting time, while small amounts even slightly shortens it. Setting time of SBR modified CAC materials can be accelerated by small amounts of Li_2CO_3.

Keywords: calcium aluminate cement, hydration, setting time, SBR latex, polymer modified mortar.

1. **Introduction**

SBR has been widely used for floor and bridge overlays. The advantages are excellent bond strength (adhesion) to numerous substrates, higher flexural strength, frost resistance, reduced shrinkage and cracking and lower permeability [**1, 2**].

Calcium aluminate cement (CAC) is very versatile special cement advantageously used in numerous specific applications [**3, 4**]. Due to their fast hardening with high early strengths even at low temperatures CAC is advantageously used for repair work of highways and airport's runways.

Duration of suitable workability of cement based materials during placement is defined by setting time. The use of adequate set regulators for each application is subject of great practical and financial interest. It is known that even a small amount of different organic and inorganic compounds show pronounced influence on setting time of CAC based materials [**4 - 8**].

Though less traditional and indirect, preferable techniques for measuring setting time are isothermal calorimetry, temperature rise and solution conductivity measurements [**7**]. Therefore, in this work a simple method of investigating cement hydration based on the measurement of temperature rise of cement pastes is employed.

2. Experimental

2.1. Materials

This paper examines the hydration of sample of commercial CAC ISTRA 40 taken from a regular production of Istra Cement International, Pula, Croatia. The cement has the oxide mass fraction composition listed in **Table 1**. Physical properties of used cement are given in **Table 2**. The main compounds are CA and ferrite phase (C_4AF-C_6AF_2), with mayenite, $C_{12}A_7$, gehlenite, C_2AS and β-C_2S as minor compounds.

To prepare the samples of pastes the additives were weighed into deionized water and hand mixed with 70 g of cement.

Table 1. Chemical composition of investigated CAC.

CaO	Al_2O_3	Fe_2O_3	FeO	SiO_2	TiO_2	MgO	SO_3	Na_2O	K_2O	Sum
39.12	37.78	13.17	2.46	4.42	1.80	0.91	0.30	0.18	0.17	100.3

Table 2. Physical properties of investigated CAC.

>90 µm, %	Blaine, cm^2/g	Specific gravity, g/cm^3	Setting time, min		Standard consistency, %	Bulk density, kg/m^3	
			initial	final		Loose	Compacted
3.71	3563	3.20	216	246	25.0	950	1776

A commercial 2Styrene-Butadiene-Rubber (SBR) (LGM d.o.o. Zagreb) in latex form was used with a solid content of 47% with 3 an nonionic surfactant and antifoaming agent in its commercial composition. Quartz sand with size of 0.5-1.0 mm and natural sand 0-4 mm are used. As a set regulator an accelerator Li_2CO_3 (Kemika Zagreb, analar grade) was used.

2.2 Methodology

In order to investigate the influence of SBR latex on the hydration of CAC the samples were prepared with a 0-20 % of polymer to cement mass ratio and a fixed water to cement mass ratio of 0.4 (the water in the SBR latex was also considered).

The plan of experiment is shown in **Table 3** for cement paste and in **Table 4** for mortar samples.

Table 3. Experimental plan for cement paste samples (indicated in percent per cement mass).

Sample	*% polymer*	*% Li_2CO_3*	*% water*
0p	0	0	40
10p	10		
20p	20		
30p	30		
40p	40		
0p2	0	0.02	
0p1	0	0.01	
5p1	5	0.01	
10p3	10	0.03	
10p1	10	0.01	
15p5	15	0.05	
15p3	15	0.03	
20p5	20	0.05	

Table 4. Experimental plan for mortar samples (indicated in percent per cement mass).

Sample	*% polymer*	*% Li_2CO_3*	*% sand* 0.5-1 mm	*% sand* 0-4 mm	*% water*
M0	0	0	300	0	40
M2.5	2.5				
M5	5				
M7.5	7.5				
M10	10				
0s	0	0	0	300	
3s	3	0			
6s4	6	0.004			
9s4	9	0.004			
6s0	6	0			
9s0	9	0			
0s8	0	0.008			
3s8	3	0.008			
6s4	6	0.004			

2.2.1. Temperature rise measurement setup

The cement paste specimens were cast in plastic containers with inner diameter $2R$ = 31 mm, height 50 mm and thickness of 0.7 mm. The mortar specimens were cast in plastic cups of 0.3 L $2R$ ~ 60 mm, height 160 mm. The containers were filled with specimens by continuously applying vibrations in order to minimize air entrapment. The thermocouple measuring end was placed exactly at the center of the container (r=0 and z=h/2). This was designed by fixing thin (1.3 mm) wooden support at the axis of the container. Paste specimens are carefully sealed with lids and insulating tape and placed vertically in the temperature controlled water bath (±0.03°C), while the mortar specimens are cured in air at room temperature, as shown in **Fig. 1 and 2**. K-type thermocouples 0.2 mm thick with grounded twisted-shielded wiring were used. An 8 channel data logger with a 20 bit resolution is used to collect the temperature measurements. It stores the entire set of temperatures once every second. The experimental data is simultaneously transferred to a PC. Cold junction temperature held at room temperature is sensed by a precision thermistor in good thermal contact with the input connectors (on thermal block) of the measuring instrument. In order to have accurate cold junction compensation a change of its temperature is kept as slow as possible.

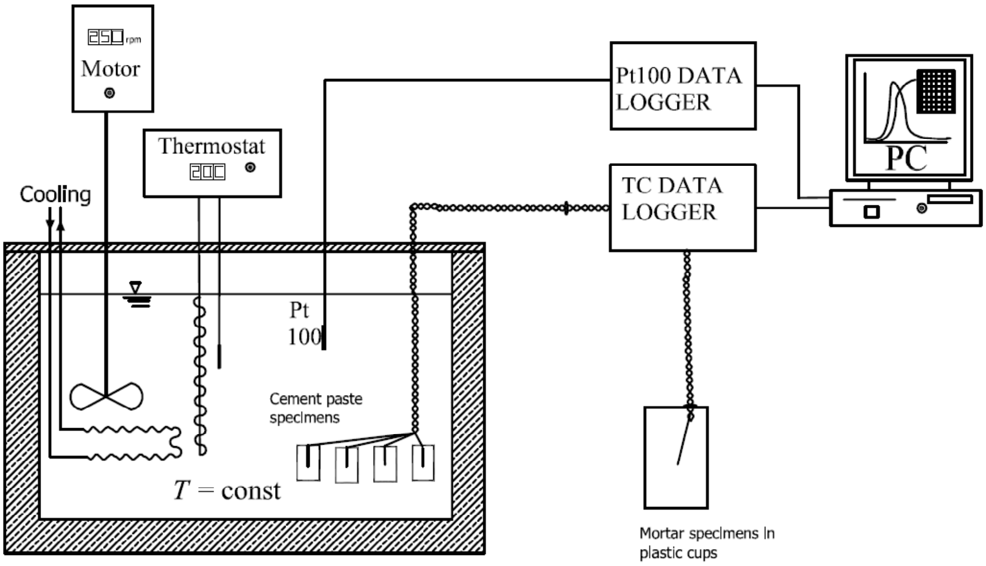

Figure 1. Scheme of the CAC temperature rise measurement setup.

No significant temperature rise is observed during the induction period of CAC hydration due to a small and constant rate of heat generation (~1 $J(h\ g)^{-1}$) [**9**]. Induction period is followed by the onset of the accelerated stage of reaction due to massive precipitation of hydrates. The maximal temperature rise is reached in only few hours after the onset of the accelerated stage.

Times of initial, t_0 and final, t_F sets can by approximated from the obtained time-temperature curves, as illustrated in **Fig 3**. In this paper the initial set is acquired from the intersection of two straight lines [**10**]: one fitted through the induction period of the curve and the other fitted through the inflection point of the rising slope of main peak. The final set was approximated as the point of maximal heat generation [**11**].

Figure 2. A photo of a) curing the mortar specimens; b) cement paste specimen hydrated in thermostated water bath.

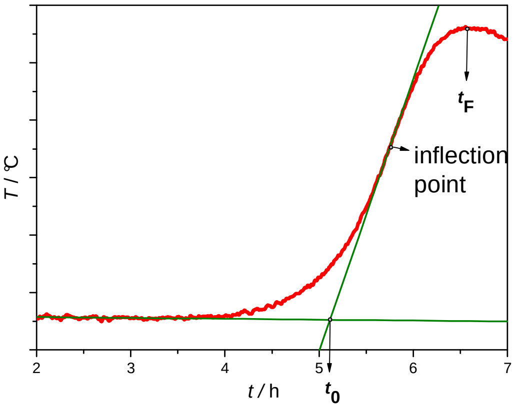

Figure 3. The method of acquiring the initial, t_0 and final, t_F setting time from temperature-time curves during hydration.

Results and discussion

Results of temperature rise measurements for CAC pastes (w/c = 0.4) cured at 4 T = 16 °C is given in **Fig 4**. It can be seen that the polymer addition significantly retards the setting time, probably due to a chemical (low level of supersaturation and sluggish nucleation of CAH_{10}) and/or physical nature (superplasticizing effect and a formation of a polymer film barrier which slows down the hydration). Interestingly, after the onset of the main peak the hydration rate is faster for the samples without the polymer. Furthermore, the flatter and longer main peak of the temperature rise curve for samples with polymer addition supports the notion of slow growth and crystallization of hydrates. No setting behavior was observed during 25 h for samples with 15 and 20 % of polymer per cement mass.

To accelerate the hydration rate and the setting time of SBR modified CAC materials small amounts of Li_2CO_3 were added. The effect of Li_2CO_3 addition on the hydration of CAC pastes is shown in **Fig 5**. More Li_2CO_3 addition results in a more rapid hydration. At the same concentrations of Li_2CO_3 the hydration is slower for higher amounts of polymers.

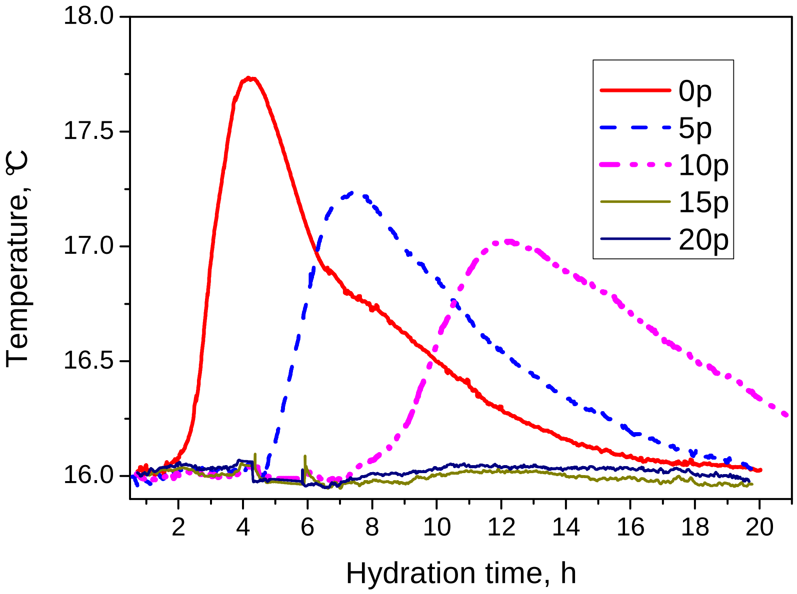

Figure 4. Temperature rise of neat CAC pastes cured at T = 16 °C.

Table 5.

Sample	t_0, h	t_F, h
0p	2.4	4.2
5p	5.0	7.5
10p	8.8	12.0
20p	- (> 25)	- (> 25)
0p2	- (< 0.4)	1.8
0p1	- (< 0.5)	1.7
5p1	- (< 0.6)	1.9
10p3	- (< 0.3)	0.6
10p1	1.2	2.6
15p5	- (< 0.3)	0.7
15p3	- (< 0.35)	0.8
20p5	- (< 0.45)	0.9
M0	3.7	5.5
M2.5	3.0	4.8
M5	3.9	6.0
M7.5	6.3	6.7
M10	7.2	9.9
0s	1.9	3.2
3s	2.0	3.4
6s4	1.5	2.7
9s4	2.0	3.8
6s0	4.7	6.9
9s0	5.2	7.4
0s8	1.5	2.8
3s8	1.6	3.3
6s4	2.7	4.3

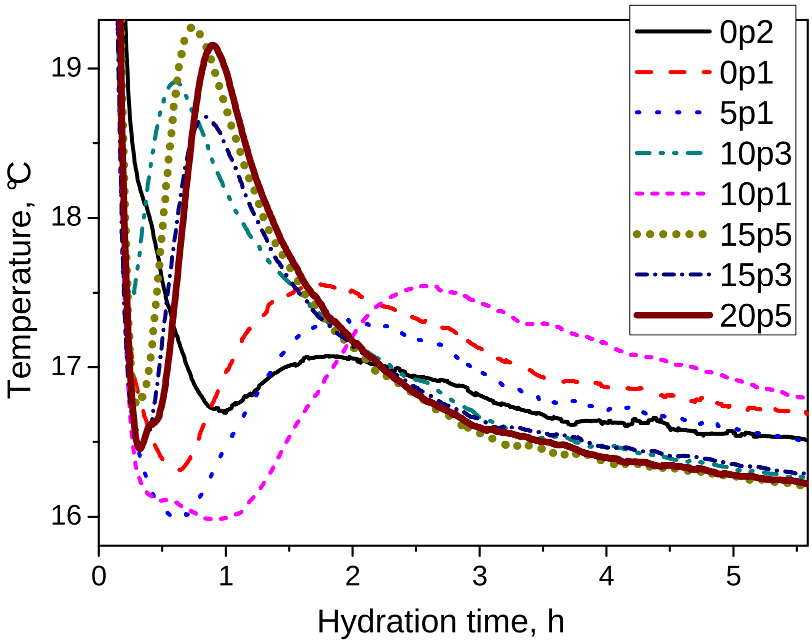

Fig. 5. Temperature rise of CAC pastes with addition of Li_2CO_3 cured at $T = 16$ °C.

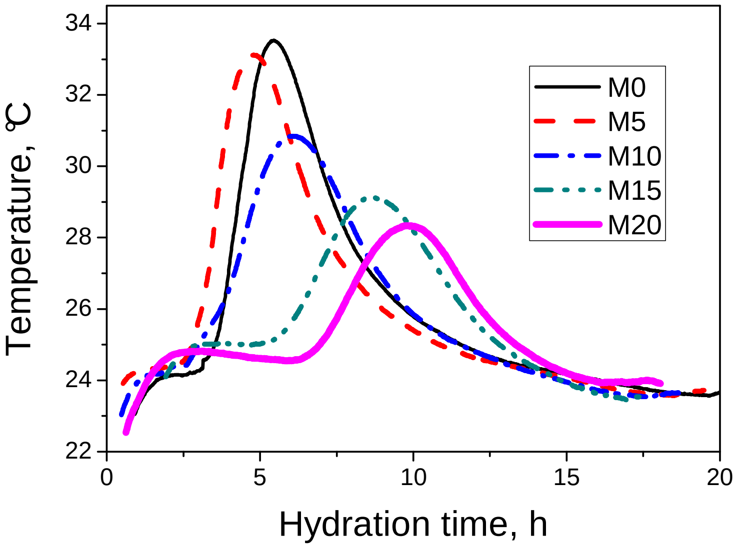

Figure 6. Temperature rise of mortar specimens cured at room temperature (sand 0.5-1mm).

Results of temperature rise measurements for CAC mortars mixed with quartz sand 0.5 - 1mm is given in **Fig 6**. It can be seen that larger SBR additions (p/c ≥ 6%) retard the setting time, while small amounts even slightly shortens it (sample M5). Samples with polymer addition exhibit a flatter and longer main peak of the temperature rise curve.

The influence of small amounts of Li_2CO_3 on SBR modified CAC 5 materials is shown in **Figs 7 and 8**. More Li_2CO_3 addition results in a more rapid hydration with a steeper and higher main hydration peak.

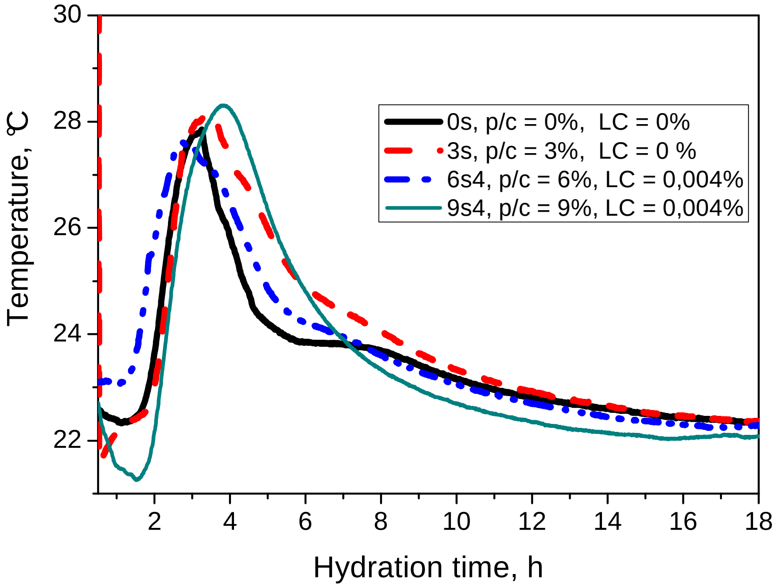

Figure 7. Temperature rise of mortar specimens cured at room temperature (sand 0-4mm), part I.

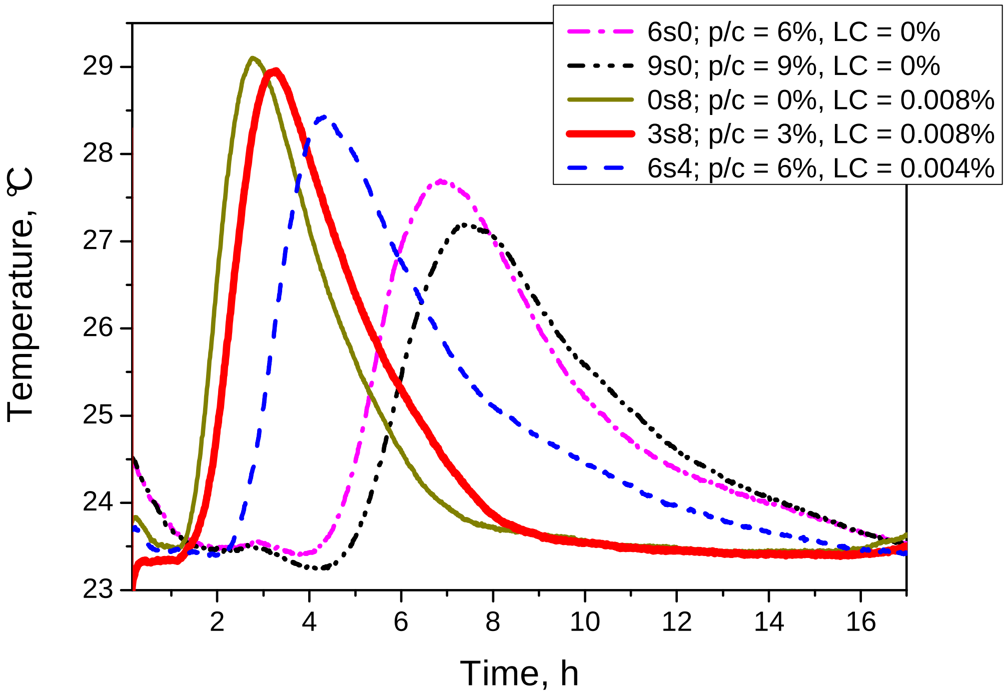

Figure 8. Temperature rise of mortar specimens cured at room temperature (sand 0-4mm), part II.

Conclusion

Styrene-butadiene-rubber 6 latex addition makes a pronounced influence on the setting time of CAC based materials. Cement paste series showed high retardation of setting time with SBR addition. Mortar series showed that larger SBR additions (p/c ≥ 6%) retard the setting time, while small amounts even slightly shortens it. The flatter and longer main peak of the temperature rise curve for samples with polymer addition supports the notion of slow growth and crystallization of hydration products.

Setting time of SBR modified CAC materials can be regulated by a small amount of Li_2CO_3.

5. Acknowledgement

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