

THE INFLUENCE OF MAYENITE ADDITIVE ON THE EARLY STAGE HYDRATION OF PORTLAND CEMENT

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INTRODUCTION

Mayenite ($C_{12}A_7$), one of calcium aluminate minerals with $C/A=1.7$, has stimulated the research interest because of its better accelerator effect-rapid hardening activity [1], oxygen mobility, ionic conductivity and catalytic properties in comparison with the other calcium aluminates [2,3]. $C_{12}A_7$ can be employed as a functional component for OPC to regulate the consumption rate of sulphates, and the amount and type of carbonate phases in hydrated products can be modified. The influence of $C_{12}A_7$ on the compressive strength of mortars mainly relates to its hydration behavior, properties of hydrated products and interactions of hydrated products between $C_{12}A_7$ and primary OPC minerals [4]. For this reason, the main objective of the present work is to determine the influence of mayenite additive on the early stage hydration of Portland cement.

MATERIALS AND METHODS

Mayenite synthesis was carried out in two stages: hydrothermal synthesis (4 h, 130 °C) and calcined (1 h, at 350 °C (CA1), 550 °C (CA2) and 900 °C (CA3)) [5]. Samples of OPC were prepared in a laboratory grinding mill by grinding cement clinker (JSC "Akmenes cementas", Lithuania) (Table 1) with a 4.5 % additive of gypsum ("Sigma-Aldrich", Germany) up to $S_a = 450 \text{ m}^2/\text{kg}$. As these reactions are exothermic, isothermal calorimetry is among the most accurate methods to monitor the global reaction process through the rate of heat production. The synthetic products were added as a partial replacement of OPC at level of 7.5 % by weight of the total cementitious material. Therefore, the water and cement ratio of all OPC samples was equal to 0.5.

Table 1. Chemical and mineralogical composition of clinker

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Loss on ignition	Insoluble particles
Amount, %	19.72	5.41	4.21	62.76	3.41	0.16	1.08	2.08	0.93	0.24
Minerals	3CaO·SiO ₂		2CaO·SiO ₂		3CaO·Al ₂ O ₃			4CaO·Al ₂ O ₃ ·Fe ₂ O ₃		
Amount, %	63.19		8.89		7.21			12.81		

RESULTS AND DISCUSSION

Table 2. Heat of cement paste with synthetic calcined additive

Katoite calcination temperature, °C	Duration of hydration, h								
	0.3	1	3	5	10	15	20	24	72
	Total heat after, J/g								
350 (CA1)	58.1	75.5	84.6	94.3	127.8	160.1	185.1	201.4	300.3
550 (CA2)	43.5	99.7	112.1	124.1	164.8	200.7	228.9	247.9	335.5
900 (CA3)	82.9	98.1	110.0	110.0	157.3	194.7	227.8	249.2	350.2
Pure OPC	3.5	6.3	10.1	16.1	53.9	97.3	136.4	157.4	247.6

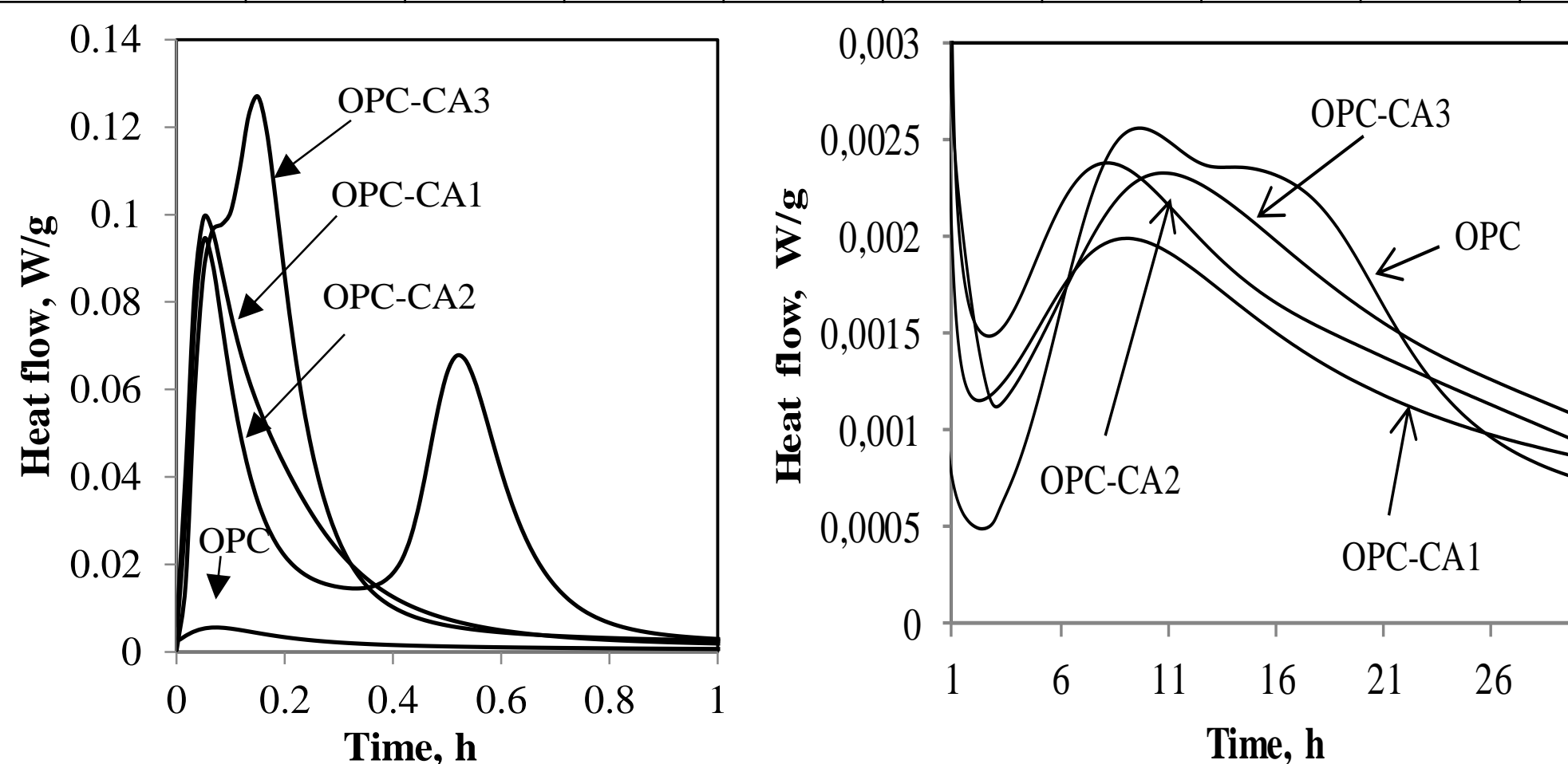


Figure 1. The heat evolution rate of OPC, OPC-CA1, OPC-CA2 and OPC-CA3 samples during the early stage of hydration.

Synthetic calcined additives accelerated the initial reaction (1-3 min) of cement samples because an increase in the maximum heat evolution rate was observed from 0.005 W/g (pure OPC) to 0.1 W/g (OPC with additives). Moreover, the new exothermic reaction was identified in the cases of OPC-CA2 and OPC-CA3. Besides, the induction period, was shortened to ~2.2 h in a case of OPC-CA1, while in pure OPC samples, the mentioned process lasted for 3 h. Moreover, the lower values of heat flow of the second exothermic reaction, typical to the dissolution of C_3S , were reached in OPC samples with additives. Meanwhile, the third exothermic reaction, which is characteristic to the dissolution of C_3A and the formation of ettringite was not identified in OPC samples with additives (Figure 1).

It was observed that in OPC samples with additives the quantity of heat released from 0 to 1 h duration of hydration was equal to 75-98 J/g, while in pure OPC samples only - 6.3 J/g. Meanwhile, in OPC-CA1 sample the quantity of heat released within the same duration of hydration was lower and equal to 75 J/g. At later stages of hydration, the calorimetric curve of all samples showed the typical hydration reactions, because the same heat increased tendency was observed (Table 2).

In order to investigate the mineralogy of compounds formed during hydration, the heat evolution experiments were repeated at 25 °C for different time periods. As expected, after 3 min of OPC samples hydration, the main diffraction peak of gypsum slightly decreased (~2 %) and traces of ettringite was identified (Figure 2, a). The different results were obtained in samples with additive: at the beginning of OPC+CA1 sample hydration (3 min) the intensity of main diffraction maximum of gypsum decreased from 2692 counts to 142 counts (Figure 2, b) while, in OPC+CA2 and OPC+CA3 it decreased to 448 and 759 cps, respectively (Figure 2).

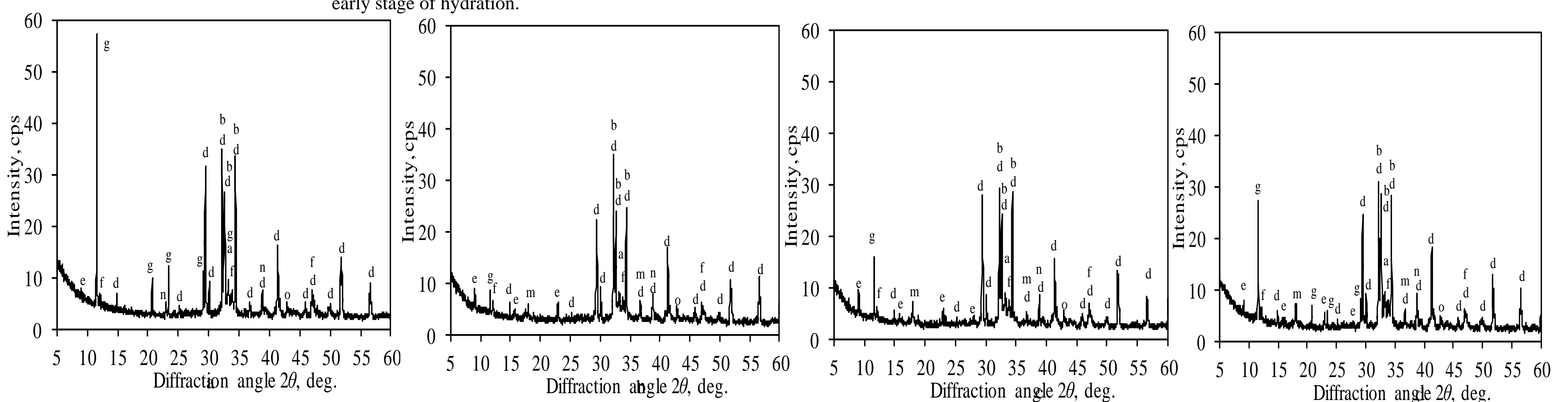
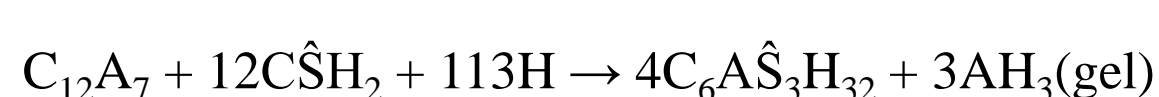


Figure 2. XRD patterns of pure OPC (a), OPC-CA1 (b), OPC-CA2 (c) and OPC-CA3 (d) samples after 3 min hydration. Indexes: e – ettringite; f – brownmillerite; a – tricalcium aluminate; b – dicalcium silicate; d – tricalcium silicate; o – periclase; n – anhydrite; m – mayenite

It was determined, that after 3 and 60 minutes of hydration, the intensities of diffraction peaks corresponding to tricalcium silicate, dicalcium silicate, brownmillerite and tricalcium aluminate in pure OPC samples were ~1.2 times higher than that in the samples with additives (figures 1-2). It was established that the interaction of gypsum and formation of ettringite depends on the reactivity of additive, and the proceeded reaction can be written as:



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