



International Conference on Ecology and new Building materials and products, ICEBMP 2016

Properties of cement pastes with zeolite during early stage of hydration

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Abstract

Properties of cement pastes with various replacement levels of natural zeolite were tested by isothermal calorimetry and rotational rheology. Zeolite from the Eastern Slovakia region was used for tests. Kinetics of exothermic reaction during early-stage of hydration were monitored by calorimetry. The role of different replacement level of zeolite on main rheological parameters is discussed in the paper. The onset point of formation of C-S-H products and the main calorimetric peak move to earlier times with increased zeolite content. Zeolite causes acceleration of hydration before the heat flow peak time and the following deceleration proportionally to its content. Zeolite in cement promotes the AFt formation, which increases the elastic response of fresh paste at the beginning of hydration. Trends of G' and phase angle show that zeolite accelerates the hydration of C_3S and early C-S-H formation.

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Peer-review under responsibility of the organizing committee of ICEBMP 2016

Keywords: Cement; zeolite; hydration; calorimetry; rheology

1. Introduction

Natural zeolites as pozzolanic material contain reactive SiO_2 and Al_2O_3 that can react with one of the Portland cement (PC) hydration products $Ca(OH)_2$ – portlandite (CH) to form C-S-H products similar to those that are formed during hydration of PC. Zeolite as supplementary cementitious material in cement is considered to be beneficial in terms of improvement in lowering the heat of hydration, durability, reduced sulfate attack and reduction in energy

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costs [1,2,3,4]. The composition of zeolite is close to endmember of Ca-heulandite in clinoptilolite-Ca – heulandite-Ca solid solution series. Heulandite as the main constituent of studied natural zeolite comprising a three-dimensional tectosilicate arrangement of silica and alumina tetrahedra with complex formula: $(Ca,Na)_2\text{-}_3Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$. Heulandite forms monoclinic crystals with a Mohs hardness of 3 to 4 and a specific gravity of 2.2. It commonly occurs as a product of devitrification of volcanic glass.

Early hydration of cement mixtures with 5%, 10% and 15% of zeolite was tested by means of isothermal calorimetry and rheometry. Complex reactions during first hours and days of hydration are essential for materials final performance and durability.

Nomenclature

AFt	ettringite
AFm	monosulfate
CH	portlandite
PC	cement CEM I 52.5N
Z	zeolite Zeocem micro50

2. Materials, methods and sample preparation

Cement pastes with various replacement level of zeolite (0 wt. %, 5 wt. %, 10 wt. % and 15 wt. %) were tested. Portland cement CEM I 52.5 N, zeolite and distilled water were used for the preparation of pastes in laboratory conditions. Water to cement ratio was $w/c=0.5$ for all samples. The composition of samples is given in Table 1. The results of chemical analyses of PC and zeolite Zeocem - micro50 done by XRF method is given in Table 2.

Rheological experiments were carried out on rotational rheometer DHR-1. The plate-plate geometry with crosshatched plates (d - 20 mm) was used for oscillatory tests. Samples were tested at 25 °C, sampling interval – 10.0 s/pt., strain – 0.01 %, angular frequency – 1.0 rad/s, gap – 2000 μm. Development of heat flow (mW) over time was monitored by means of isothermal calorimetry at 25 °C. The temperature during testing was controlled by the Peltier system.

Table 1. Composition of samples.

Sample	PC 52.5N	Zeolite – Zeocem micro 50
	(wt. %)	
C	100	-
C 5% Z	95	5
C 10% Z	90	10
C 15% Z	85	15

Samples of cement pastes for rheological tests were prepared by hand in laboratory glazed dish. Measurement started 5 minutes after adding water. The amount of tested sample was given by the 2 mm gap between plates. Samples for isothermal calorimetry were tested in AdMix 20 ml ampoules. Ampoules with 4 g of dry sample were tempered, then the water was injected into ampoule using the syringe and the sample was mixed by vane impeller. Measurement started in a few seconds after adding the water. Particle size distribution done by CILAS 920L of Portland cement and zeolites is shown in Table 3.

Table 2. Chemical composition of Portland cement and zeolite.

	CEM I 52.5N	Zeolite – Zeocem micro 50
	(wt. %)	
SiO ₂	24.01	34.63
SrO	0.03	0.11
MnO	0.22	0.01
TiO ₂	0.32	0.52
K ₂ O	0.77	2.55
Na ₂ O	0.26	0.26
SO ₃	3.26	1.51
MgO	2.67	0.77
CaO	64.48	41.72
Fe ₂ O ₃	2.97	3.61
Al ₂ O ₃	7.42	29.27

Table 3. Particle size distribution of PC and zeolites.

	CEM I 52.5N	Zeolite – Zeocem micro 50
Diameter at 10 % (μm)	1.17	2.08
Diameter at 50 % (μm)	8.76	8.46
Diameter at 90 % (μm)	21.69	28.30
Mean diameter (μm)	10.36	12.20

3. Results and discussion

3.1. Isothermal calorimetry

Isothermal calorimetry allows precise and accurate measurements of heat flow development in time. Thanks to isothermal conditions during measurement it is possible to detect all exothermic reactions related to hydration of fresh cementitious materials. Four main exothermic peaks can be seen on the calorimetric curve.

The first peak with the proportionally large signal is attributable to initial wetting and dissolution reactions and rapid reaction of aluminates phase C₃A with sulfates from clinker and gypsum (CaSO₄·2H₂O) which is traditionally added as the retarder of setting. Ettringite (AFt, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) is formed as a main crystalline product at this stage. Amorphous hydrates with the composition of AFt along with crystalline AFt are formed. Disorganized “gel-like” layer of hydrates around C₃A particles that is responsible for slowing down the reaction was described by several authors [5,6,7]. C₃S also partly reacts during initial hydration [8]. Zeolite is the other source of reactive alumina. This fact can be seen on intensities of the first peak. Intensities grow with the increase of zeolite content (Fig. 1). The nucleation effect of zeolite smallest particles cannot be excluded. Nevertheless, smallest particles of zeolites are coarser compared to those of PC.

The period of slow reaction between initial peak and the second “silicate peak” gives information about workability time. The second peak is related to nucleation and growth of C-S-H hydrates and CH. Mechanisms that were proposed [9] are still controversy on the topic of the start of acceleration period. The rate of hydration in acceleration period, as an analogy to autocatalytic reactions, depends on the amount of C-S-H products [9,10,11]. The onset point of the second peak at the beginning of acceleration period corresponds to the start of the setting and the maximum of the second peak to the end of setting and start of hardening. In the case of cement mixtures with zeolites the position of the onset point and the maximum of the second peak move to earlier times accordingly to the increase of replacement level of zeolite (Fig. 2). The advance of the onset of the acceleration stage is related to the

adsorption of Ca^{2+} on the pozzolan either as a surface layer or as C–S–H. This mechanism would allow the C_3S to dissolve more rapidly through a thinner or less dense layer of C–S–H growing on the C_3S grains [12].

The third and the fourth peak can be monitored in the deceleration period where the hydration process is diffusion controlled. The process of hydration is slowed down during this period due to consumption of small particles, leaving only large to react, lack of space and water. The third peak sometimes described as a shoulder of the second peak is related to renewed formation of AFt after depletion of gypsum. The timing of this peak that is controlled by dosage of gypsum was found to be very important in terms of resulting strength of the hardened material. Lerch [13] proposed that best strengths are achieved when the third peak is approximately 2-3 hours after the second “silicate” peak. At this time, AFt grows in hardening material but there is still space for needle-like crystals to grow in the porous structure and thus, make the material more compact. Intensities of the third peak are decreasing and the positions of the third peak are moving slightly to later times with increase of zeolite content.

The fourth peak is accompanied with exothermic reaction during recrystallization of AFt to one of the phases of AFm group (monosulfate, hemicarbonate or monocarbonate aluminate hydrate). Kinetics of reaction in deceleration period of hydration is slowed down accordingly to the replacement level of zeolite. The intensities of the fourth peak are decreasing and their positions are moving to later times with increasing content of zeolite.

Total heat development (Fig. 3) shows that up to peak time that is roughly after 12 hours of the hydration is accelerated by the presence of zeolite. Total heat values are very similar for all the mixtures regardless of zeolite content at the heat flow maximum after 12 hours of hydration. Similar trend was observed in previous work [14]. On the other hand, there is significantly slower heat development after the peak time in deceleration period due to zeolite. Acceleration before the peak time and following deceleration of the heat development is proportional to the replacement level of zeolite.

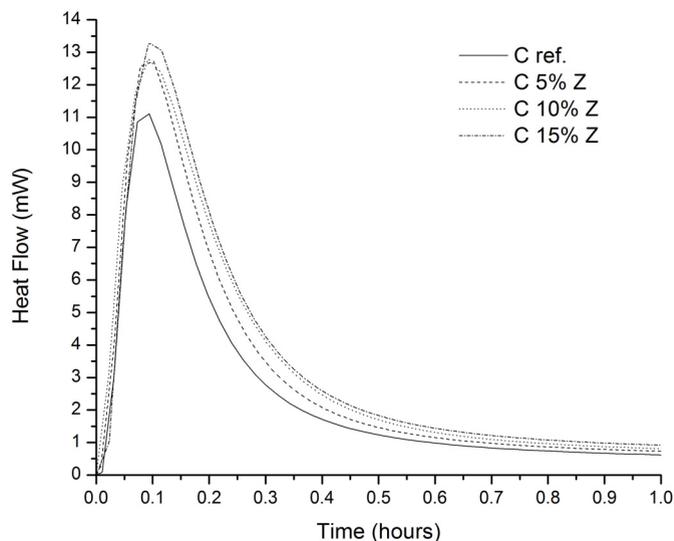


Fig. 1. Initial peak of cement.

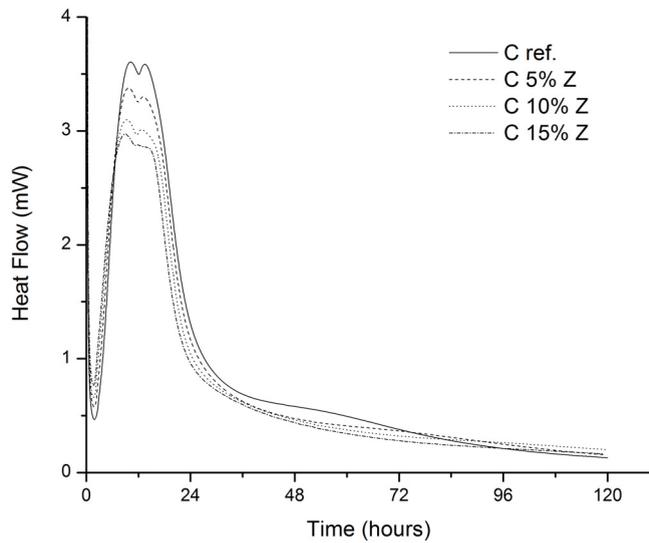


Fig. 2. Heat flow development.

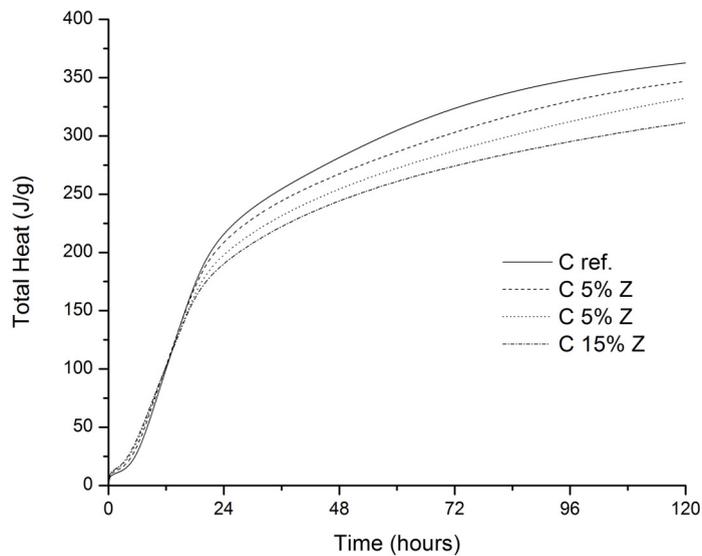


Fig. 3. Total heat development.

3.2. Rheology

The change in rheological parameters was studied by oscillatory tests on rotation rheometer during early hydration. Elastic modulus G' and phase angle ($^\circ$) were monitored continuously until the start of the setting.

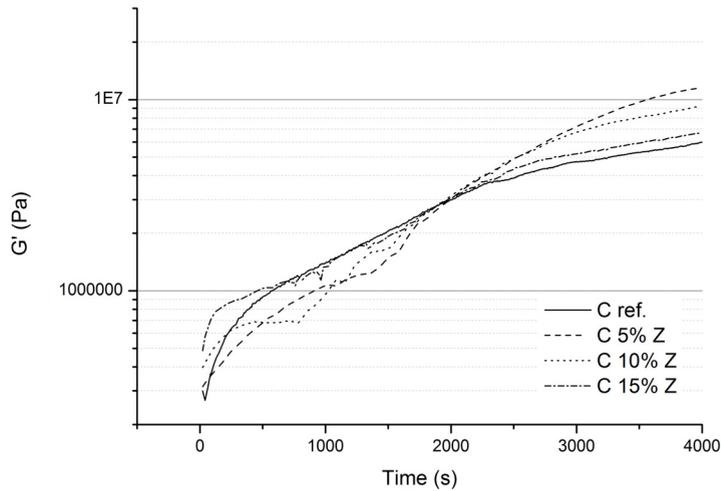


Fig. 4. Elastic modulus (G')/time dependence during early hydration

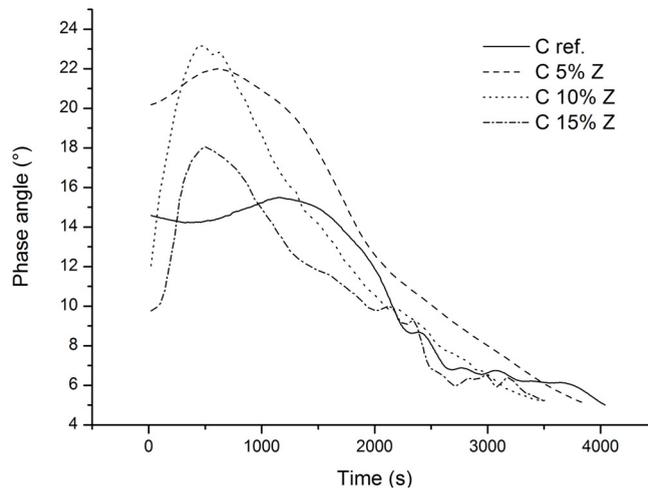


Fig. 5. Phase angle/time dependence during early hydration.

Rheological parameters follow the structural changes that material undergoes during setting. Zeolite as an admixture modifies the hydration process and consequently the rheology of the fresh paste.

Zeolite increase the elasticity of the paste at the very beginning due to promoted formation of AFt. The amount of AFt formed and its morphology is influenced by the rate of CH and gypsum dissolution in the liquid phase [15]. The formation of AFt is increased as the saturation of the liquid phase with CH is low due to the presence of zeolite [16]. The formation of AFt is also promoted by reactive alumina from the zeolite.

Nucleation effect of zeolite particles must be taken into account. The previous study confirmed enhanced consumption of C_3A and C_4AF during early hydration in cement mixtures with chabazite-clinoptilolite based zeolite. The lower crystallinity of the zeolite would probably allow an increased adsorption of Ca^{2+} and possibly explains the difference in C_3S hydration [17]. This is probably one of the reasons for higher rates of C_3S hydration in the presence of zeolite. The very start of the setting is characterized by an increase of G' and a decrease of phase angle values to approximately 5° . At this stage G' and phase angle values reveal the start of the setting. Higher values of G' with the increased level of zeolite proved that zeolite accelerates the hydration of C_3S and thus the formation of C-S-H products.

4. Conclusions

The position of the onset point of formation of C-S-H products and the maximum of the main “silicate” peak move to earlier times with increased replacement level of zeolite. Intensities of the third peak related to renewed formation of AFt and fourth peak related to AFt to AFm recrystallization are decreasing and their position is moving slightly to later times with increase of zeolite content. Acceleration of hydration before the heat flow peak time and the following deceleration is proportional to zeolite content. The presence of zeolite in cement promotes the formation of AFt which results in the increase of the elasticity of the fresh paste at the beginning of hydration process. Trends of G' and phase angle proved the acceleration role of zeolite on the hydration of C_3S and early C-S-H formation.

Acknowledgements

This paper was elaborated with the institutional support for the long-term development of research organizations by the Ministry of Industry and Trade of the Czech Republic and with the support of the project Sustainability and Development REG LO1211 addressed to the Materials Research Center at FCH VUT.

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