

Early-stage hydration heat development in blended cements containing natural zeolite studied by isothermal calorimetry



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ABSTRACT

Early-stage hydration heat development in blended Portland cement-based binders containing natural zeolite in an amount of up to 40% by mass is investigated using an isothermal heat flow calorimeter. Experimental results show that the presence of natural zeolite in the blended binders accelerates the onset of C_3S hydration and boosts the first phase of C_3A hydration. The second phase of C_3A hydration gains on importance in the hydration process with the increasing zeolite dosage. For the zeolite contents higher than 30%, the maximum specific hydration heat power in this phase is even higher than the maximum corresponding to the C_3S hydration. The effectiveness of the natural zeolite as a binder, as expressed by the difference specific hydration heat per 1 g of zeolite, is found to decrease with its increasing dosage in the blends. The replacement of Portland cement in an amount of 10% by mass by natural zeolite can be considered as a limit for its effective use. Above this limit, a substantial part of zeolite does not directly participate in the hydration process and plays a role of a fine filler instead. The limited zeolite participation in the blended-cement hydration can explain the lower compressive strength of zeolite concretes containing higher amounts of natural zeolite, which was reported before.

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1. Introduction

Zeolites are natural volcanic or synthesized aluminosilicate minerals with typical microporous framework structure. Thanks to their high specific surface, they are widely used mainly in chemical engineering as catalyst support [1], molecular sieves [2], or sorbents [3], but their utilization as pozzolans dates back already to ancient times when the mixture of zeolites containing tuff and lime was used as hydraulic binder [4]. The actual research and utilization of zeolites as cement admixtures was obviously focused on naturally occurring minerals which are exploited in several countries, e.g., China [5], Turkey [6], Greece [7], or Slovakia [8], but considerable attention has also been paid to recycling of spent zeolite catalysts from petrochemistry [9,10].

Natural zeolites, similarly to other pozzolans, are taking part in hydration reactions and can contribute to the strength of cementitious materials. Perraki et al. [7] reported a good pozzolanic reactivity of zeolite, 0.555 g of $Ca(OH)_2$ per 1 g of zeolite according to the Chapelle test. Poon et al. [5] and Chan and Ji [11] found out that the pozzolanic activity of zeolite was lower than silica fume but

higher than fly ash. Ahmadi and Shekarchi [12] observed a positive effect of cement replacement in mortars by zeolite on compressive strength and resistance to alkali-silica reaction. The positive influence of zeolite on concrete sulfate corrosion was reported by Janotka and Krajci [13]. Najimi et al. [14] found that incorporation of 15% natural zeolite improved strength and durability properties of concrete. Bilim [15] and Sisman and Gezer [16] recommended a 5% cement replacement by natural zeolite. Karakurt and Topçu [17] reported an increased durability of concrete containing zeolite as partial Portland cement replacement. Therefore, zeolite obviously has a good potential as supplementary cementitious material in concrete.

The effect of natural zeolite on the early hydration of Portland cement was investigated by various methods in the past. Perraki et al. [7] and Kontori et al. [18] studied the hydration rate and products of Portland cement pastes with natural zeolite dosage within a range of 10–30% by means of X-ray diffraction and Fourier transform infrared spectroscopy, in a combination with thermogravimetry and differential thermal analysis. Poon et al. [5] determined the degree of reaction of zeolite in the cementitious system by a selective dissolution procedure using picric acid-methanol solution and water. Snellings et al. [19,20] applied for the analysis of early-age hydration of zeolite-blended cements the synchrotron X-ray powder diffraction method.

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The time development of hydration heat of blended cements containing zeolites which belongs to the main characteristics of the early-stage hydration process was studied very rarely in the past. Su et al. [9], Pacewska et al. [10], and Garca de Lomas et al. [21] studied the early-age hydration heat of Portland cement blended with spent zeolite catalyst in an amount of up to 35% of the mass of cement but the composition of the applied catalysts was significantly different from natural zeolite. Snellings et al. [22] analyzed the hydration heat development in natural zeolite samples mixed with portlandite in a 1:1 ratio. However, the measurements of early-stage hydration heat characteristics of blended cements containing natural zeolite were not reported yet in relevant literature sources.

This paper presents –in our knowledge for the first time – the early-age hydration heat development in blended cements containing up to 40% of natural zeolite as Portland cement replacement. The experiments are performed using isothermal calorimetry which can – contrary to most other methods – provide directly the heat generation rate, thus achieve a higher measurement accuracy than, e.g., the adiabatic or semiadiabatic methods. The measured dependence of the hydration heat production on time is applied for the identification of the effectiveness of natural zeolite as a binder in terms of its participation in the hydration process, depending on its amount in the blended binders. In this way, some irregularities in the measurements of mechanical properties of zeolite concretes containing different amounts of zeolite, which were reported before, can be explained.

2. Materials

Blended cements were prepared using Portland cement CEM I 42.5 R. The chemical composition of cement as determined by the XRF analysis is shown in Table 1. The specific surface area of cement measured by the Blaine method was 336 m²/kg. The natural zeolite from the mining area in Nizny Hrabovec, Slovakia consisted of clinoptilolite (84%), cristobalite (8%), glimmer (4%), rutile (0.1–0.3%) and traces of quartz; its chemical composition is given in Table 1. The specific surface of zeolite determined by the Blaine method was 852 m²/kg, the total surface obtained using the BET method was 30,655 m²/kg. The particle size distribution of Portland cement and zeolite as measured by a laser particle size analyzer is presented in Fig. 1.

In the blended binders used at the preparation of cement pastes for the hydration heat measurement, 10, 15, 20, 30, and 40% of mass of Portland cement was replaced by natural zeolite. Portland cement without any admixture was used as well, for the sake of comparison. The water/binder ratio was 0.50 in all cases. The analyzed cement pastes will be denoted as PC (Portland cement), CZ10, CZ15, CZ20, CZ30, CZ40 (cement with the zeolite replacement level of 10–40%), in what follows.

Table 1
Chemical composition of natural zeolite and cement in mass %.

Component	Natural zeolite	CEM I 42.5 R
SiO ₂	74.7	18.3
Al ₂ O ₃	15.0	4.9
Fe ₂ O ₃	1.5	3.7
CaO	3.3	66.0
MgO	0.7	1.1
K ₂ O	3.6	0.9
Na ₂ O	0.8	0.1
TiO ₂	0.2	0.3
SO ₃	–	4.2

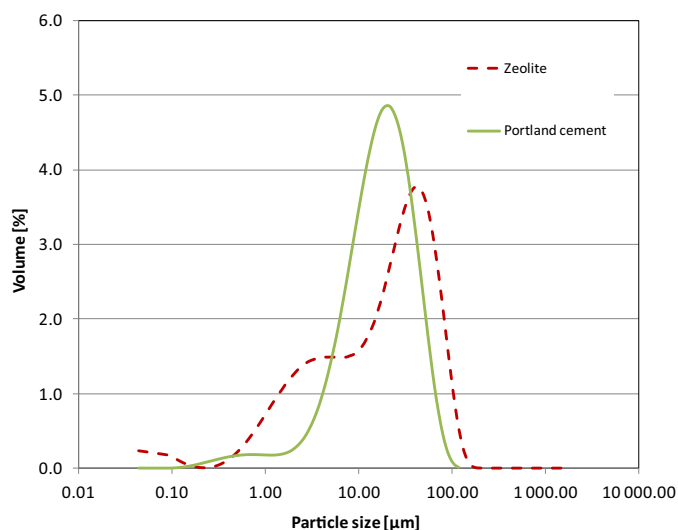


Fig. 1. Particle size distribution.

3. Experimental method

The isothermal heat flow calorimeter KC 01 [23] was applied for the measurement of hydration heat development in the analyzed blended cements. The device is based on the differential measurement of heat flow. Detectors for the heat flow measurement are constructed in the form of copper-constantan thermocouple columns, which are wound up on an insulator plate. The thermocouple joints are placed on the edges of the plate and glued to a copper tube which a cylinder copper reaction vessel with the specimen of about 1–2 g is inserted into. The detectors on the tube where the hydration process takes place are connected differentially with the detectors for determination of heat flow at the reference vessel where no hydration processes occur. The vessels and detectors are arranged in an axial symmetric way. Data collection is performed using a datalogger with the signal detection range of 0–100 mV and sensitivity of 0.01 mV. The collected data is then transferred from the datalogger to PC and processed. In the measurement of temperature inside the calorimeter a resistance thermometer with the sensitivity of 0.01 °C is used.

The calibration of the KC 01 calorimeter was carried out on the Joule heat principle, using a resistor with the precisely known resistance of 9.99 kΩ placed into the reaction vessel and powered by regulated DC power supply. The voltage was measured by a high-accuracy digital voltmeter. In the range of 0–100 mW, the applied power was found to be proportional to output voltage of the differentially arranged thermocouple columns, with the calibration constant of 16 mW/mV at 25 °C.

The measurement was performed with a 1.5 g sample of Portland-zeolite cement paste in a cylindrical copper vessel of inner diameter 10 mm and height 70 mm, with a tight rubber plug. In the process of sample preparation, Portland cement and zeolite were mixed at first. The great differences in their fineness required a different way of mixing than usual. The weighted amounts of the two components were mixed together in a little polyethylene bag by hand. The bag was put into the copper vessel of the calorimeter in horizontal position to prevent gravitational segregation of the components due to their different density. After inserting the copper vessel with the solid sample into a stabilized calorimeter, a weighted syringe with water has been placed near the reaction vessel, and so was a plastic tubule intended for paste mixing. The calorimeter with the solid sample and water was left to stabilize the temperature. After about 1 h stabilization, the calorimeter was opened and water was inserted in the vessel. The paste was mixed

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