

Properties of mixtures of cement with various raw materials

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Abstract. This paper presents possibility of utilization of selected Czech and Slovak industrial and natural raw materials in blended cement production. The cement blends were prepared using 75 wt. % of cement and 25 wt. % of a substituent. The paper is focused only on test results of the laboratory-prepared blended cements. The influence of admixture on hydration process was observed by calorimetric measurement of heat evolution during hydration process within 24 hours. The hydration products of water-cured samples for 28 days were determined by thermal analysis. Further properties, such as short and long-term compressive strengths and setting period, were determined.

1. Introduction

The possibility of utilization of wastes or non-traditional raw materials in cement production is discussed all around the world. Portland cement industry is responsible for approximately 5% of global CO₂ emission [1]. Partial replacement of Portland cement by one or more additives to obtain blended cements is generally associated with significant savings in energy and cost and it also supplies more durable cementitious systems to construction industry. Nowadays, the range of building materials is extended and various blended cements are produced using fly ash, slag or mineral admixtures, which is documented in the EN 197-1 standard. By replacement of Portland cement or clinker by such secondary raw materials, a satisfactory quality of cement can be still reached, moreover, some advantageous properties can be obtained, such as a decrease of hydration heat, specific rheological and setting properties etc. [2, 3].

Recently in Turkey, a complete research on natural pozzolans such as zeolites and volcanic tuffs was conducted [4]. Natural pozzolans show excellent ability to reduce the alkali-silica expansion and they provide many beneficial properties of both fresh and hardened concrete [5]. Whereas natural pozzolans tend to increase the water ratio requirement for concrete, their use in blended Portland cement is generally limited by 30%. In Greece, the effect of other natural pozzolan – diatomite – on blended cement properties and on hydration process was studied as well. Blended cements, having up to 10% of diatomite content, develop the same compressive strength as corresponding Portland cement [6, 7]. It was proven that an effective mineral additive can be manufactured by thermal activation of raw kaolin with at least 41.6% of kaolinite [8], the thermally activated kaolin is very effective admixture in blended cements based on high strength. A long-term research of fly ash, slag and silica fume utilization has confirmed their suitability for the blended cement production.

This work is focused on properties of 8 secondary and non-traditional materials (2 samples of fly ash, 2 samples of slag, 2 samples of rock and 2 samples of other material) selected from a group of 59 monitored materials from the Czech Republic and Slovakia. Their suitability of utilization in composite cements is observed.



2. Materials and methods

Cement blends were prepared from Portland cement CEM I 42.5 R and selected industrial and natural raw materials in the ratio 3:1 by mass. Chosen raw materials were: fly ash, fluidized ash, ground granulated blast-furnace slag (GGBS), foundry slag, marlite, zeolite and two silica fumes. Before mixing with cement, every material except silica fumes was milled in laboratory ball mill so that the residue on 0.09 mm sieve was 2–3%. The basic characteristics of these raw materials are given in Table 1.

Table 1. Basic monitored components in raw materials in wt. % determined by X-ray diffraction and their specific surface.

Raw material	Specific surface m ² /kg	Amorphous content wt. %	Free CaO wt. %	Other parameters
Fly ash	649	73.4	-	-
Fluidized ash	1256	55.2	6.6	-
GGBS	195	83.9	-	-
Foundry slag		0.0	-	high content of belite
Marlite	681	22.9	-	contains opal
Zeolite	1211	43.0	-	clinoptilolite, heulandite, opal
Silica fume I	1187	100.0	-	-
Silica fume II	4041	100.0	-	-

X-ray diffraction of raw materials was performed on Bruker D8 Advance apparatus with Cu anode ($\lambda K\alpha = 1.54184 \text{ \AA}$) and variable divergence slits at Θ - Θ Bragg-Brentano reflective geometry. Quantitative phase analysis was done by Rietveld method using software Topas. Amorphous phase was quantified by addition of internal standard (20 wt. % of CaF_2).

The influence of admixture on hydration process was observed by calorimetric measurement. Heat released during hydration process was measured within 24 hours. The hydration products of water-cured samples for 28 days were determined by thermal analysis. Further properties, such as short and long-term compressive and flexural strengths and setting process, were determined.

Observation of the course of the temperature during hydration process of prepared blended cement pastes was performed on isoperibolic calorimeter [9]. The measurements were carried out for 24 hours at 35°C.

The setting process of prepared cement blends, containing industrial and natural raw materials, was observed by a Tussenbrock method. Tussenbrock method is performed on a device with a needle similar to Vicats. Depth of submersion of six cylindrical probes of decreasing diameter in the cement paste is measured in time dependence. The depth of indentation of particular probe indicates a threshold of shearing stress (in kPa) which corresponds to consistency achieved at the moment of measurement. This method allows to capture several anomalies during the setting process such as false setting.

Compressive strengths were measured in mortars from blended cements containing industrial and natural raw materials prepared according to EN 196-1 standard, water-cured for 2, 7, 28, 56 and 90 days. Mortars were prepared according to standard, i.e. with binder to sand ratio 1:3 and water to cement ratio $w/c = 0.5$.

The hydration products of blended cement pastes were determined by means of the differential thermal analysis. The samples from calorimetric measurement, water-cured for 28 days, were crushed to grain size of 1–5 mm, rinsed by ethyl alcohol and acetone and dried. The samples were then ground to grain size less than 0.09 mm and subjected to DTA-TG measurement on the Netzsch Perseus STA 449 apparatus in temperature range of 20–1000°C. This method in some cases enables to quantify the processes related to thermal decomposition of hardened cement (when peaks do not overlap each other).

3. Results and discussion

3.1. Technological properties

Figure 1 compares the hydration process of samples containing admixtures to the reference sample of ordinary Portland cement. Except the fluidized ash, all replacements of cement by different admixtures result in a reduction of hydration heat and temperature maximum of hydration. A shorter time needed for the maximal temperature is achieved when fluidized ash, marlite, zeolite and silica fume were used. Other blends show a slower hydration in the comparison with the reference sample. A very slow development of hydration heat was observed in the case of foundry slag blend. The fast increase and high temperature of fluidized ash hydration process is probably caused by a content of free lime. Similar results are also observed by other authors [10]. Silica fume hydration process is influenced mainly by its fineness and the amount of used water [11]. In our experiment, amount of water is the same for all samples, therefore finer silica fume shows a delay in hydration because of not sufficient water content.

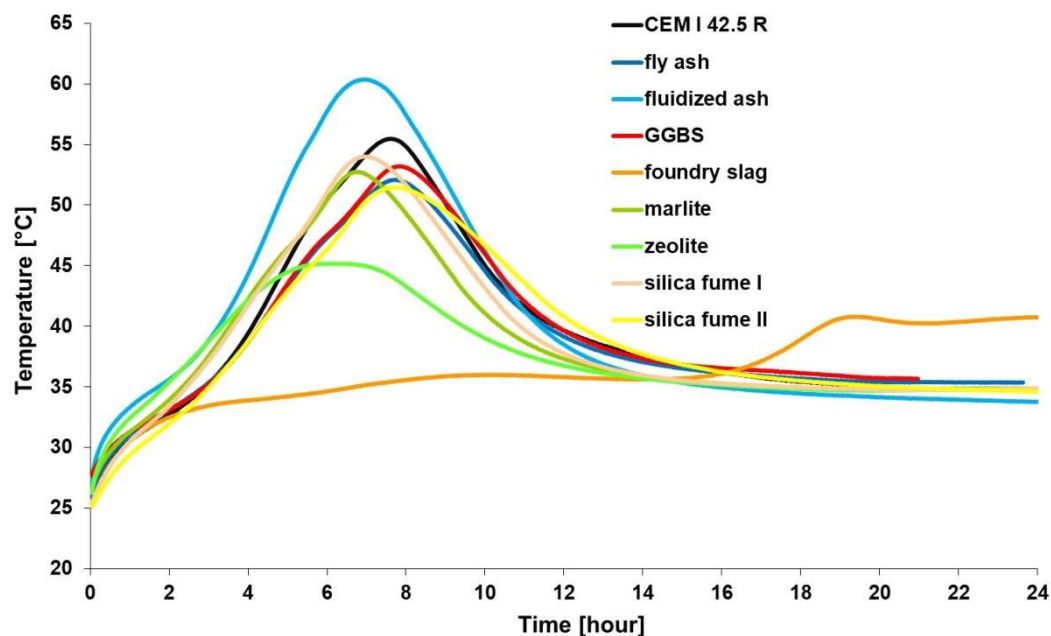


Figure 1. Hydration process of cement blends containing industrial and natural raw materials.

Figure 2 shows results of the blended cement setting process observed by means of the Tussenbrock method. The setting process of cement blends with fluidized ash, marlite, zeolite and silica fume is faster in comparison with the reference sample. This fact is in accordance with results of hydration properties mentioned above. The longest setting process was recorded for the blend with foundry slag. No signs of the false setting were recorded among prepared cement blends.

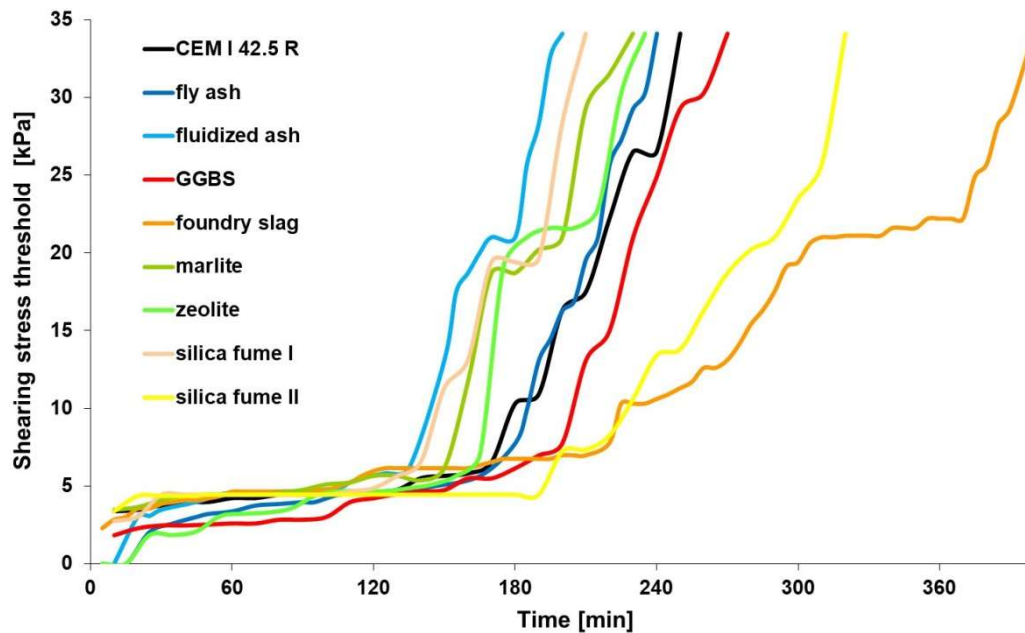


Figure 2. Setting process of cement blends containing industrial and natural raw materials.

The compressive strength data for 2, 7, 28, 56 and 90 days of hydration for blended cements and reference cement are plotted in Figure 3. All blended cements exhibit lower early strengths after 2 and 7 days. The reduction in early strengths was considerable especially in the case of foundry slag and silica fume II samples. After 28 days of aging, blends with fluidized ash and zeolite possessed a little higher compressive strength than reference CEM I. Admixtures as fly ash, silica fumes show the positive effect on the cement hydration process (good activity) after 56 days of aging. Finally, after 90 days also sample with fly ash shows comparable strengths. The lowest values of strengths were recorded for cement blend with foundry slag. By the amount of constituent in prepared cements, this cement blend can be categorized as a type CEM II according to EN 197-1. Based on the strength development of cements with fly ash, fluidized ash and silica fume I, these cements remain in strength class 42.5R as reference CEM I. Cement containing granulated blast furnace slag, foundry slag, marlite, zeolite and silica fume II belong to strength class 42.5N. From this point of view, the worst cement with foundry slag is better than for example CEM II prepared from natural pozzolan Turkish trachyandesite that belongs to strength class 32.5R [12].

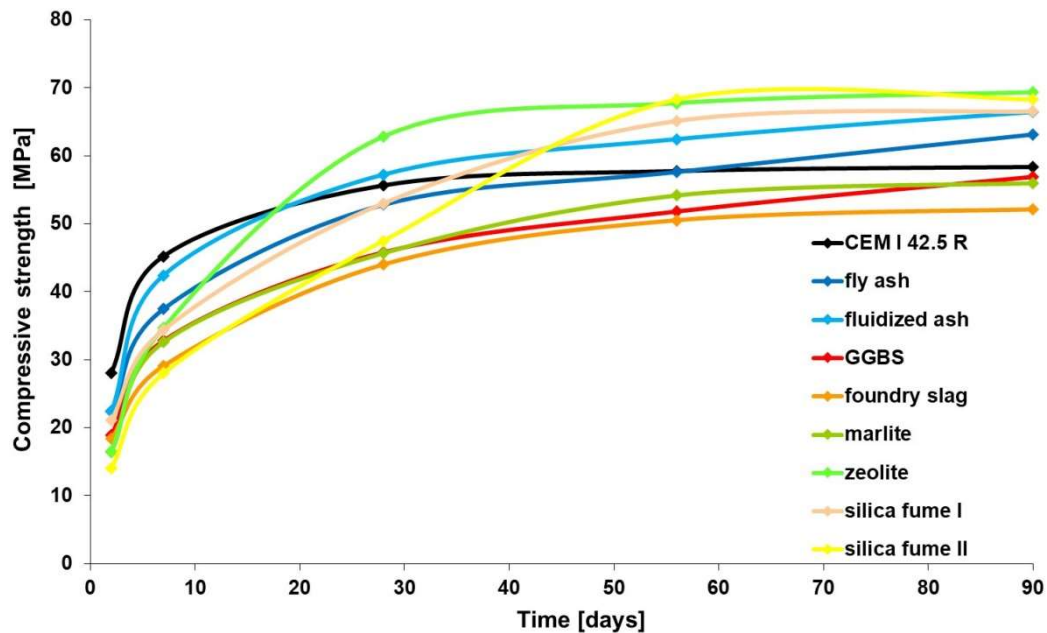


Figure 3. Compressive strengths of cement blends containing industrial and natural raw materials.

3.2. Hydration products

Four basic endothermal processes were observed in thermograms of hydrated blended cement samples. The first endotherm with minimum at 150–180°C covers several consequential and overlaying processes which include physically bonded water release and calciumhydrosilicates, ettringite or gypsum dehydration. The smaller and the least endotherm follow with the minimum at 390–430°C, which belongs to dehydration of calciumhydroaluminates. Here the $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ phase was selected for quantity evaluation. The next significant endotherm around 540 °C is related to portlandite $\text{Ca}(\text{OH})_2$ dehydroxylation. The last endotherm with the minimum at 800–900°C defines the calcite CaCO_3 decarbonation. The quantitative evaluation of hydration products is given in Table 2.

Table 2. Quantitative evaluation of cement pastes, water-cured for 28 days, by DTA in wt. % (*overlapping of processes, ** Loss on ignition).

Cement blend with:	Hydrate H_2O	C_3AH_6	$\text{Ca}(\text{OH})_2$	CaCO_3	LOI**
CEM I 42.5R	10.1	4.9	12.6	12.5	20.0
Fly ash	10.0	5.0	2.7*	14.9*	18.6
Fluidized ash	9.8	3.4	7.5	10.2	17.2
GGBS	11.5	5.2	8.8	10.6	19.8
Foundry slag	10.2	4.3	10.5	10.8	18.8
Marlite	11.5	4.3	6.6*	19.1	22.8
Zeolite	13.8	4.7	8.1	9.5	21.3
Silica fume I	12.3	5.0	4.7*	12.0	20.0
Silica fume II	16.9	5.7*	2.4*	10.2*	23.5

4. Conclusions

The results show that the hydration reactions within observed blended cements proceed in various ways and do not necessarily indicate the final strengths. The phase composition and microstructure of raw materials could be the reason for this phenomenon. The most significant factors are fineness of raw materials and content of amorphous phase, in case of fluidized ash also the amount of free CaO.

Compared to the reference sample, the best values of long-term compressive strengths along with comparable hydration process were obtained in cement blends with silica fume II and zeolite as admixtures.

Zeolite decreases the hydration heat development, keeping the compressive strengths still quite high due to its pozzolan character and it seems to be a suitable admixture in the amount of 25 wt.% for a blended cement production. It is necessary to pay attention to a possible increased mixing water demand. The mixing water demand can differ from type to type and may be the cause of lower short-term strength rate.

Samples with fly ash and fluidized ash showed increased heat development during first 24 hours, and reached similar, relatively high long-term strengths.

Strong delay of initial setting and low hydration heat, yet satisfactory long-term strength can be observed in the sample containing foundry slag.

Acknowledgements

This paper was elaborated with the Institutional support for long-term development of research organizations by the Ministry of Industry and Trade of the Czech Republic.

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