DIFFERENTIAL SCANNING CALORIMETRY OF HIGH-PERFORMANCE CONCRETE WITH BURNT CLAY SHALE ADDITION

Trník A.[1,2,*], Scheinherrová L.[2], Medved' I.[1,2] and Černý R.[2]
*Author for correspondence
[1]Department of Physics, Constantine the Philosopher University, 94974 Nitra, Slovakia
[2]Department of Materials Engineering and Chemistry, Czech Technical University, 16629 Prague, Czech Republic
E-mail: atrnik@ukf.sk

ABSTRACT

Mineral additives are used in concrete primarily due to a positive effect on its mechanical properties. Using the differential scanning calorimetry, it is possible to observe thermophysical changes in concrete samples containing such additives at the microstructural level. In our study high-performance concrete samples with a different mass% of a burnt clay shale addition were prepared. The burnt clay shale is a pozzolana active material which can be used as a partial replacement for the cement binder. The aim of this paper is to investigate the hydration and pozzolanic reaction in a high-performance concrete with the burnt clay shale addition using differential scanning calorimetry (DSC) and thermogravimetry (TG). The investigation was performed in the temperature range from 25 to 1000 °C with a heating rate 5 °C/min in an argon atmosphere.

INTRODUCTION

High-performance concrete can be produced from an ordinary Portland cement or a blended cement combined with other materials as a supplementary cementing material [1]. Such materials are, for example, fly ash, grounded granulated blast-furnace slag, silica fume, or natural pozzolans (such as metakaolin) [2, 3]. This type of addition may be called an active pozzolanic material which reacts with water when it is used with lime or cement. This chemical reaction has a positive impact on the properties of concrete [3]. The pozzolanic material is defined as a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in a finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties [4].

Pozzolans are naturally occurring minerals as well as industrial by-products [5]. Their production has not so high environmental impacts as in the case of concrete (producing CO_2 emissions, consumption of resources and energy by their production) and the price is relatively low [6, 7]. The use of minerals containing amorphous silica (pozzolans) reduces the amount of calcium hydroxide (Portlandite) in the hardened paste, because they react with $Ca(OH)_2$ which is generated by the cement hydration. This behavior is beneficial because pozzolans produce a more strength-giving material and some amount of Portlandite can be leached out during chemical attack. During hydration of concrete calcium silicate hydrate gel (C-S-H), which reduces the porosity of the binder and makes the substance more compact, is formed [8, 9]. In addition, the fine grains allow a denser packaging in the cement and they have a positive effect on the reduction of the wall effect in the transition zone between the paste and aggregate. This zone is strengthened due to a higher bond between these two phases, which improves the concrete microstructure and properties [9].

There have been many studies of hydration of cement with different pozzolana. The hydration, relative strength and pozzolanic activity were studied by Wild and Khatib [10]. They determined that there are three elementary factors which affect the contribution that metakaolin makes to concrete strength in the case that it partially replaces cement – the filler effect, the acceleration of ordinary Portland concrete hydration, and the pozzolanic reaction of metakaolin with $Ca(OH)_2$. They also defined the optimal replacement level of ordinary Portland cement by metakaolin to obtain a maximal long-term strength enhancement to be about 20 %.

The effect of metakaolin on the hydration process of Portland cement cured at low temperatures 5 – 20 °C for 3 – 28 days were studied using thermogravimetric analysis [11]. They identified the hydration products decomposing at specific temperatures. It was determined that metakaolin also accelerates Portland cement hydration at low temperatures 5 – 10 °C.

More results on the effect of metakaolin during the hydration process are given in the studies [12-15]. The hydration process was described using different pozzolana, such as silica fume [16, 17], fly ash [18-21], natural pozzolana

[22, 23], or using waste materials which have pozzolanic properties [24-27].

In this paper a specific type of clay shale with a large amount of kaolinite is studied by the differential scanning calorimetry (DSC) and thermogravimetry (TG). The clay shale is extracted from several areas which are mostly close to the pit coal mines [28]. This type of pozzolana is usually used in the natural form for the production of refractory ceramics and in the burnt form as grog in the ceramic industry. The clay shale has pozzolanic properties after burning at temperatures similar to those when kaolinite is transformed into metakaolin (500 – 700 °C). While this new type of pozzolana was already studied as a partial replacement of binder in lime composites [28], here we wish to investigate its hydration and pozzolanic reaction in a high-performance concrete when it is burnt at 750 °C.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The samples of high-performance concrete were prepared from Portland cement (CEM I 52.5 R, according to the EN 197-1 standards), burnt clay shale labeled as L_{05} (from České lupkové závody Corp., Nové Strašecí, Czech Republic), natural quartz, and basaltic sand (its continuous granulometry was 0 – 4 mm), silica fume, superplasticizer, and water/cement ratio of 0.21, which was chosen to achieve the lowest porosity.

Table 1 The chemical composition of the burnt clay shale

Component	Amount (%)
SiO_2	52.90
Al_2O_3	41.90
TiO_2	1.80
Fe_2O_3	1.08
K_2O	0.77
MgO	0.18
CaO	0.13
LOI	1.24

The composition of pozzolanic burnt clay shale is given in Table 1. This material was used as a partial replacement of the cement binder from 0 to 60 %. Six types of samples with a different amount of pozzolana were chosen to study the effect of the burnt clay shale on the properties of high-performance concrete. The composition of the studied materials is shown in Table 2. The detailed preparation procedure of the concrete was described in [29].

Experimental methods

For the study of the hydration and pozzolanic reaction in the high-performance concrete with a burnt clay shale addition we used the differential scanning calorimetry and thermo-gravimetry. For our measurements finely ground samples were prepared which were placed into an alumina crucible with a volume of 100 mm^3. All experiments were realized in the temperature range from 25 to 1000 °C with a heating rate 5 °C/min in an argon atmosphere and were repeated three times for each sample type. As blank curves, we used data from a second measurement of the same material under identical conditions. Therefore, any reversible processes that take place in the material cannot be registered in these two thermal analyses.

EXPERIMENTAL RESULTS AND DISCUSSION

In Figure 1 we show the DSC thermogram of the pure burnt clay shale powder which contained no admixtures. The only peak is at the temperature ~968 °C with the enthalpy of 47.88 ± 1.1 J/g. This temperature and enthalpy were averaged from three separate measurements. The peak corresponds to the collapse of the metakaolinite lattice and a subsequent formation of spinel [30, 31].

The results for the samples with a different amount of burnt clay shale are given in Figures 2 and 3. The heat flow (in mW/mg) and relative mass change (in %) at a given temperature is shown in the figures for all studied samples. In Figure 2 several heat flow peaks occur. The size of these peaks varies with the amount of the burnt clay shale.

The heat flow peaks in the temperature interval from 25 to 250 °C (see Figure 2) correspond to the liberation of physical bound water from pores and also to dehydration reactions due

Table 2 The composition of the studied high-performance concrete in kg/m^3

Material	CEM I 52.5 R	Clay shale	Silica fume	Silica powder	Natural quartz and basalt sand				Superplasticizer	Water
					0.1 – 0.6	0.3 – 0.8	0.6 – 1.2	1.0 – 4.0		
BP3-10	585	65	148	148	440	281	219	159	30	170
BP3-20	520	130	148	148	440	281	219	159	30	170
BP3-30	455	195	148	148	440	281	219	159	30	170
BP3-40	390	260	148	148	440	281	219	159	30	170
BP3-50	325	325	148	148	440	281	219	159	30	170
BP3-60	260	390	148	148	440	281	219	159	30	170

to loss of water from C-S-H gel [8]. These peaks are visible for endothermic peak is present; it belongs to the ettringite decomposition [8]. The higher the amount of the bunt clay shale, the larger the peak is. The reactions in this temperature interval are also connected with a significant mass loss (see Figure 2). For the sample with 10 mass% of the burnt clay shale it is about 3.9 %. The mass loss decreases with an increasing amount of the burnt clay shale, and it is about 3.3 % for the sample with 60 mass% of the burnt clay shale.
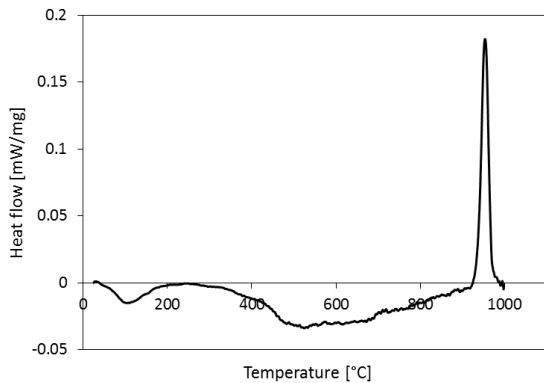

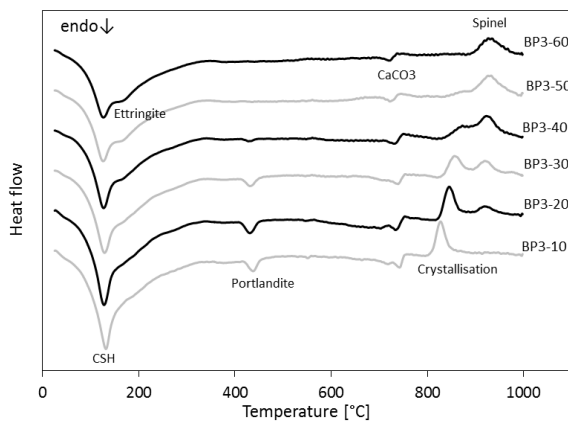**Figure 1** The DSC thermogram of the pure burnt clay shale

Figure 2 The DSC thermograms of the high-performance concrete containing 10 – 60 % of the burnt clay shale replacement

The next peak is in the temperature range from 400 °C to 480 °C and it is connected with the dehydration of Ca(OH)2 (Portlandite). The dehydration is also accompanied by a mass loss. This effect is the most visible for the material with a lower amount of the burnt clay shale. For the sample with 10 mass% of burnt clay shale it is about 0.3 %, and it decreases with the amount of the burnt clay shale.

The next relevant temperature for our studied material is 573 °C. At this temperature the $\alpha \rightarrow \beta$ transformation of quartz takes place. This reaction is accompanied by a sharp endothermic heat flow peak and a volume change (about +0.68 % [32]). However, in Figure 2 this reaction is not visible because it is reversible and, as pointed out earlier, it cannot be detected in the measurements. During the quartz transformation

there is no change of mass. The small peak in the sample with 10 mass% of the burnt clay shale at the temperature about 570 °C is visible but is caused just by an inaccuracy of measurement.
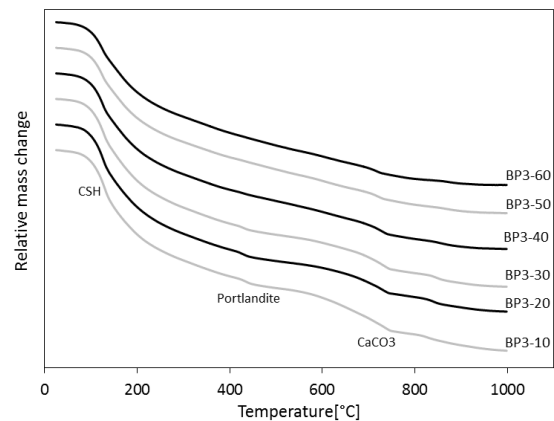

Figure 3 The relative mass change of the high-performance concrete containing 10 – 60 % of the burnt clay shale replacement

After reaching the temperature 750 – 770 °C, the $CaCO_3$ decomposition is initiated. This effect is accompanied by a more significant mass loss than in the case of the $Ca(OH)_2$ dehydration. This fact is valid for the materials with the lowest amount of the burnt clay shale.

At temperatures above 800 °C, there are two exothermal peaks. One peak corresponds probably to the crystal growth of cubic MgO [33] or to the crystallization of akermanite [34]. The other peak corresponds to the formation of spinel in the burnt clay shale [30, 31]. The first effect is visible for the samples with the amount of the burnt clay shale less than or equal to 40 %, but it is not at the same temperature. The temperature of this peak increases with amount of the burnt clay shale. The second heat flow peak is not at exactly the same positions for all samples as in the case of the burnt clay shale itself. The heat flow peak is moved in the higher temperatures (about 950 °C) at materials with higher amount of the burnt clay shale. For the sample with 10 mass% of the burnt clay shale is not visible.

Enthalpy results

For the several phases occurring in the high-performance concrete we determined the enthalpy of their peaks (see Figure 2). The results are given in Table 3. The peaks corresponding to the liberation of physically bound water and the decomposition of C-S-H gel and ettringite are not studied.

The results show that with an increasing amount of the burnt clay shale the temperature and enthalpy of peaks are changing. The first studied peak was associated with the Portlandite dehydration. The temperature of the peak and enthalpy of this reaction decrease with the amount of the burnt clay shale. This peak vanishes in the materials if the amount of the burnt clay shale is more than 40 mass%.

The second studied peak corresponds to the calcite decomposition. The results are similar as for the Portlandite dehydration. So, the temperature and also enthalpy of this

Table 3 The enthalpy results for the corresponding peaks in the high-performance concrete containing various amount of the burnt clay shale

Material	Portlandite dehydration		Calcite decomposition		Crystallization		Spinel formation	
	Temperature	Enthalpy	Temperature	Enthalpy	Temperature	Enthalpy	Temperature	Enthalpy
	°C	J/g	°C	J/g	°C	J/g	°C	J/g
BP3-10	453.08	3.52	758.03	18.85	840.05	12.63	–	–
BP3-20	448.94	3.90	752.58	17.85	863.80	12.36	937.90	3.29
BP3-30	447.88	2.78	755.78	8.18	873.91	8.07	936.62	4.71
BP3-40	446.82	0.70	751.30	4.13	889.68	1.55	940.08	6.72
BP3-50	–	–	743.44	2.84	883.50	0.45	945.26	11.39
BP3-60	–	–	742.55	2.47	–	–	942.98	11.81

reaction decrease with the amount of the burnt clay shale till it completely vanishes.

The third peak which was investigated is associated with the crystallization. We observe that the temperature of the crystallization shifts to higher values, and thus the enthalpy decreases as the amount of the burnt clay shale increases. For sample containing 60 mass% of the clay shale the reaction does not occur.

Finally, the fourth peak corresponds to the formation of spinel. This time both the temperature of the reaction and the associated enthalpy increase with the amount of the burnt clay shale. However, for the sample containing 10 mass% of the clay shale the spinel formation is practically negligible.

Note that the peaks for the two latter reactions – crystallization and spinel formation – become overlapping for the samples with the amount of the clay shale larger than 30 mass%. Consequently, the determination of the enthalpy in these cases could be somewhat inaccurate.

CONCLUSION

In this paper we studied high-performance concrete samples with a different addition of burnt clay shale. The aim was to investigate the hydration and pozzolanic reaction using differential scanning calorimetry and thermogravimetry in the temperature range from 25 to 1000 °C. We determined the temperatures and enthalpies of four individual reactions that occur in the samples: the Portlandite dehydration, calcite decomposition, crystallization, and spinel formation. Moreover, we investigated the influence of a varying amount of the burnt clay shale on these reactions. Namely, we showed how the reactions' temperatures and enthalpies change (increase or decrease) due to this amount.

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