

The calorimetric observation of hydration processes of alkaline activated granulated blast furnace slag

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Abstract Development a new alternative binder systems is realized by alkaline activation technogenic pozzolana materials. In comparison with common Portland cement have these materials many advantages such as high strength, low cost production and long-term durability. The aim of this work is to evaluate the hydration process by calorimetric measurement. Is assess calorimetric curve of sample alkali activated granulated blast furnace slag and sample of Portland cement. The thermal effect of hydrated mixture was monitored by isothermal microcalorimeter Tam Air.

1 Introduction

Knowledge of the effects of various thermal processes is important not only for practical applications, but also for thermodynamic calculations. Calorimetric method direct determination thermal effects of different process. To understand the different calorimetric methods and functions of the various calorimeters is the best description watched process and the conditions which this process takes [1].

Each calorimetric device has three basic parts:

1. calorimetric own container or cell (calorimeter) where is monitored process,
2. sensor is in thermal contact with the cell and measure physical quantity A which reflects thermal changes in cell,
3. shell is define as area around the calorimeter (mostly thermostat) [1].

2 Methods a data

For the thermodynamic description of observe process and quantitative evaluation of size thermal effect is particularly necessary knowledge of timing of the variable A . Is necessary to know:

- a) the timing of the calorimeter temperature T_k (if that is not directly elected for the observed quantity A),
- b) the timing of progress temperature T_p ,
- c) the constant of proportionality K between the size of the thermal effect q (quantity of heat absorbed or released) and the value (or change) measured value A or in general functional dependence of q a A , $q = f(A)$,
- d) a constant heat transfer between the calorimeter and the shell k , which determines the amount of heat exchanged between the calorimeter and the shell per unit time for unit temperature difference [1].

If ongoing process in the calorimeter, in which the released per unit time (or consume) the quantity of heat dq/dt changes the measured value A at the same time unit for dA/dt . At the same time exchanges heat between the calorimeter and shell. The amount of heat exchanged between the calorimeter and the shell is proportional to the difference in temperature and per unit time is given by $(dq/dt)=k(T_k - T_p)$. The relationship between variables is following formula:

$$\frac{dq}{dt} = K \frac{dA}{dt} + k(T_k - T_p) \quad (1)$$

The parameters K and k are generally independent of temperature (not constant), but in a narrow range of temperature can be considered as constants [1].

When sorting thermodynamic calorimeters can be assumed, how in during process change variables T_k and T_p and what physical quantity A is measured. Device can be categorize to approximately into three groups described below (see **Tab. 1**) [1].

Tab. 1 Groups of calorimeters

Type calorimetry		The relationship between T_k and T_p	Characteristic symbol
Isothermal	own isothermal	$T_k = T_p = \text{const.}$	$A \neq T_k, (q_{\text{vym}} = 0)$
	isodiathermic	$T_k = \text{konst.}, T_p = \text{const.}$	$T_k > T_p, A \neq T_k, (dq/dt = \text{const.})$
Adiabatic	own adiabatic	$T_k = T_p = f(dq/dt)$	$A = T_k$
	adiathermic	$T_k = f(dq/dt) \neq T_p = \text{const.}$	$k = 0, A = T_k$
Diathermic		$T_k = f(dq/dt), T_p = \text{const.}$	$k \neq 0, A = T_k$

During isothermal measurement is own calorimetric cell maintained at constant temperature. The temperature of the shell is also constant and often identical with the temperature of the calorimeter, and so throughout the measurement is no heat transfer between the calorimeter and shell [1].

Isothermal heat is possible to determine the colour of very fast events or processes whose speed can be regulated (eg. evaporation, mixing, dissolving, etc.). During the measurements have to guaranteed perfect compensation of thermal effects and have to remove variations of temperature T_k . Otherwise it could lead to uncontrolled heat transfer to the surroundings and it would greatly reduce the accuracy of the results [2].

A typical way to test of different cement mixtures in small scale is to use method of calorimetry, the science of measuring the heat of chemical reactions or physical changes of system. Cement mixtures have to tendency loosen heat exothermically that is proportional to the rate of cement hydration [3].

3 Experiential and results

Two compounds were make. The first mixture contains of granulated blast furnace slag (GBFS), which was activated by water glass and included the addition of distilled water. The second mixture consists of cement (CEM 42,5 R), which was activated with distilled water. Alkaline activator (water glass) was adjusted to silicate module $MS = 2,00$ and dose in quantities 4.5 wt.% Na_2O due to dry ingredients.

3.1 The raw materials used

Primary raw materials used for the experiment were granulated blast furnace slag, cement, alkaline activator (water glass) and distilled water.

Blast furnace slag was produced from company ArcelorMittal Ostrava a.s. and was granulated in own factory. Grinding was made by Kotouč Štramberk al. s.r.o.. Next material was cement (CEM 42.5 R) produced by a.s. Cement Hranice with high quality fast setting and with maximum 5% of additional components.

3.2 Used equipment calorimetric

Air isothermal calorimeter has eight channels designed for sensitive and stable measurement of thermal flow. It is ideal device for large-scale calorimetric experiments that require a response in the mW. It can operate in temperatures ranging from 5 to 60°C with a variation $\pm 0.02^\circ\text{C}$. Connecting a computer enable to automate of measurements and summary results.

Both mixtures were recorded during 48 hours thermal flow and heat. The composition of mixtures is shown in **Tab. 2**.

Tab. 2 Composition of mixtures

Mixture	Number	Distilled water	Water-glass	Total
1 – CEM 42,5 R	5 g	1,5 g	0 g	6,5 g
2 - GBFS	5 g	0,4 g	1,4 g	6,8 g

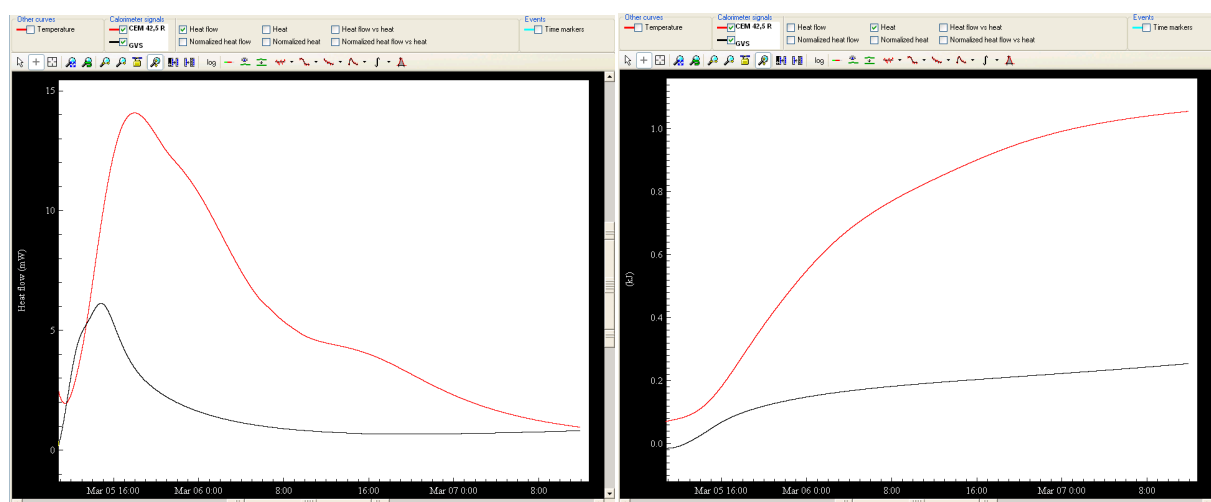


Fig. 3 Calorimetric curve of thermal flow and heat in GBFS (black) and CEM (red)

4 Discussion

In **Fig. 3** is showed a calorimetric curve the thermal flow and heat in GBFS (black) and CEM I 42,5 R (red). In CEM I 42,5 R is apparent rapid evolution of heat, in GBFS is see a slow development of heat. Decrease of curve is interrelate with finish development of heat and cooling of reaction mixture. Comparison of calorimetric thermal flow curve and heat developed during hydration samples shows a rapid increase in thermal flow sample CEM I 42,5 R, which slowly decrease against sample GBFS. The observed dependence is caused by the exothermic



reaction of the hydration phases present in the samples. Phase composition of each types of raw material is different. Composition of Portland cement is composed of 35 to 65 wt% C_3S^1 , 10 to 45 wt% C_2S , about 10 wt% C_4AF , 3 - 15 wt% C_3A , up to 10 wt% glass phase and about 2 wt% CaO . All crystalline phases are involved in processes of hydration immediately after mixing with water. In the case of blast furnace slag, the situation is different. Slag is formed glass phase consisting of approximately 40 wt% CaO and SiO_2 , and the same amount of approximately 8 wt% Al_2O_3 . Due to the alkaline activator effect occurs when the slag to break Si-O, Al-O and Ca-O bonds. Is assumed that over a solution leads to formation of new hydration products. They are both in the case of hydrated Portland cement and slag activated. The dominant are compounds of the general composition of $C_x-S_y-H_z$ (so called CSH) phase. Unlike hydrated Portland cement no contains portlandit - $Ca(OH)_2$ which is easily corrode component. against activated slag [4]. The peak of thermal flow CEM I 42,5 R is 14 mW. Peak of thermal flow GBFS is 6 mW, it is less than half of CEM I 42,5 R. Calorimetric thermal curve documents the course of temperature increase. In CEM I 42,5 R is see rapid development of heat up to maximum 1,1 kJ. In GBFS is slow development of heat only 0,3 kJ which corresponds to the aforementioned differences in phase composition.

5 Conclusion

The aim of this study was monitored hydration calorimetric processes of alkali-activated granulated blast furnace slag and cement. For this purpose, was used isothermal microcalorimetr Tam Air. From the above Fig. 3 shows that the calorimetric curves of each mixtures are different in incerease of temperature in the mixtures, the time achiaive of maximum temperature and maximum value this temperature.

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Literature

- [1] KALOUS, V. a kol. *Metody chemického výzkumu*. 1. vyd. Praha: SNTL, 1987. 430 s.
- [2] Schmidt, M. *Kalorimetrie* [online]. 2006. cit [2012-29-3]. Dostupné na WWW: <eso.vscht.cz/cache_data/40/www.vscht.cz/ktt/.../kalorimetrie.pdf>.
- [3] OBERLINK, A., ROBL, T. *Non-portland cement activation of blast furnace slag*. 2011 World of Coal Ash (WOCA) Conference, 2011, Denver, Co, USA, <http://www.flyash.info/>
- [4] VLČEK, J. Materiálové využití strusek z metalurgie železa a oceli metodou alkalické aktivace. *Habilitační práce*. Ostrava: VŠB-TU Ostrava, 101 s., 2008.

¹ Marking usual in the ceramic, where C is CaO , S SiO_2 , H is H_2O , A is Al_2O_3 , F is Fe_2O_3 , example C_3S is $3CaO \cdot SiO_2$