Construction and Building Materials 64 (2014) 333–341

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Investigation on early hydration of ternary Portland cement-blast-furnace slag–metakaolin blends

Martin Boháč [a,*], Martin Palou [a], Radoslav Novotný [a], Jiří Másilko [a], Dalibor Všianský [b], Theodor Staněk [c]

[a] Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno, Czech Republic
[b] Masaryk University, Faculty of Science, Department of Geological Sciences, Kotlářská 267/2, 611 37 Brno, Czech Republic
[c] Research Institute of Building Materials, JSC, Hněvkovského 65, 617 00 Brno, Czech Republic

HIGHLIGHTS

- Initial hydration of PC–BFS–MK ternary system is influenced mainly by PC and MK.
- MK accelerates the hydration of clinker minerals.
- The third peak on calorimetric curve is related to formation of hemicarbonate.
- Hemicarbonate is formed as a product of conversion of ettringite.

ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form 6 March 2014
Accepted 1 April 2014
Available online 4 May 2014

Keywords:
Ternary system
Portland cement
Metakaolin
Blast-furnace slag
Hydration

ABSTRACT

The paper investigates the hydration of ternary blends comprising Portland cement, blast-furnace slag and metakaolin. The isothermal calorimetry and "in situ" X-ray diffraction was used to evaluate the effect of metakaolin and blast-furnace slag on the early hydration of blends. XRD, DTA and SEM were used to analyze the hardened paste after 1 month of hydration. Metakaolin influences significantly the kinetics, mechanism and products of hydration at initial period of hydration causing the rapid formation of ettringite. Hemicarbonate aluminate hydrate is formed as a product of ettringite conversion due to the presence of reactive calcite in Portland cement.

1. Introduction

Binary blends of Portland cement (PC) with one of the supplementary materials, such as blast-furnace slag (BFS), fly ash (FA), silica fume (SF), finely ground limestone (L), and metakaolin (MK) are well known and widely developed and used in civil and engineering constructions [1–5]. For reason of energy cost savings (high energy consumption in cement production), environmental protection (reduction of CO_2 emission) and specific technical requirements (durability, resistance to sulfate attack or carbonation) clinker in cement should be partially replaced, wherever possible by latent hydraulic or pozzolanic materials [6–8]. In the last decades, ternary blended cements are gaining in intensity as new progressive construction materials [9–11]. However the development of self-compacting concrete and high-performance cements [12,13] often require the combination of two or more binder materials. Furthermore, particle size composition of these materials, superplasticizers [12–15] and other parameters play important role in their development. It was proved that partial replacement of PC by BFS and MK or FA and MK could be perspective for the future construction materials [1]. Both BFS and MK are used very commonly as hydraulic latent and pozzolanic material in mortar and concrete, and have showed influence in enhancing mechanical properties and durability of mortar and concrete [1]. Metakaolin MK ($Al_2Si_2O_7$–$Al_2O_3{\cdot}2SiO_2$ or AS_2), is a supplementary cementitious material with pozzolanic properties obtained by calcination of high kaolinite ($Al_2Si_2O_7 2H_2O$) content clay at temperature between 500 °C and 800 °C [16,17]. According to the literature, the research work on metakaolin is focused on two main areas. The first one deals with study of the kaolin structure, conversion of kaolinite to metakaolinite using analytical techniques for the thorough examination of kaolin thermal treatment [16–18]. The second one concerns the pozzolanic behavior of metakaolin

* Corresponding author. Tel.: +420 541 149 449; fax: +420 541 211 697.
E-mail addresses: bohac@fch.vutbr.cz (M. Boháč), palou@fch.vutbr.cz (M. Palou), novotny@fch.vutbr.cz (R. Novotný), masilko@fch.vutbr.cz (J. Másilko), dalibor@sci.muni.cz (D. Všianský), stanek@vustah.cz (T. Staněk).

http://dx.doi.org/10.1016/j.conbuildmat.2014.04.018
0950-0618/

and its effect on cement and concrete properties [19]. The properties of MK as a pozzolanic material have been reported previously [1,5,6]. MK on reaction with CH in the presence of water produces C–S–H products and alumina phases C_4AH_{13}, C_2ASH_8 and C_3AH_6 or $C4AH_{13}$ [6,20,21]. The formation of crystalline products depends mainly on the AS_2/CH ratio and reaction temperature [5–7]. Another supplementary worldwide used in cement and concrete industry is BFS, by-product of the manufacture of pig iron. Slagging agents (e.g. coke ash and limestone) are used during the process of reducing iron ore to iron to remove "impurities" as molten slag (consisting primarily of silicates and aluminosilicates of calcium and other bases) that floats on top of the molten iron. Then, it is recuperated and cooled rapidly to ambient temperature by different cooling techniques to get high glass content. The water quenching technique of the molten slag gives granulates that are finely ground to final product called ground granulated blast-furnace slag (GGBS). It is classified as a latent hydraulic material, meaning it has pozzolanic and cementitious properties after activation. It is well established the mechanism of slag alkali activation through pozzolanic reaction with calcium hydroxide released during the hydration of PC to form additional hydrated products. Ternary blend system including PC, BFS and MK can have some improved properties. Addition of BFS along with MK can improve flowability of fresh cement mixtures which is poorer due to presence of MK [13].

The purpose of the study is to analyze the effect of MK and BFS on early period of hydration of ternary blend system with PC. Mixtures of PC with different replacement levels of MK and BFS were submitted to hydration. The results of calorimetric measurements were compared with those of X-ray diffraction "hydration in situ" technique in order to assign the changes in phase composition to exothermic peaks.

2. Experimental

2.1. Materials and methods

All the materials used in this study are from Czech production. Portland cement CEM I 42.5 R is produced by Českomoravský cement, plant Radotín (Heidelberg Cement). Relatively high content of MgO in PC is due to partial dolomitization of Paleozoic limestone that was one of the raw materials for clinker burning. This limestone was used also as minor additional constituent in the cement. Reactive alkaline BFS with 78% of glass content from Moravia Steel, JSC, Třinec was used for mixtures. MK Mefisto K05 was produced in České lupkové závody, JSC, Nové Strašecí. Mostly amorphous MK contains little amount of silica, corundum and anatase. Ultrafine powder MK has its median particle size around 5 μm. The chemical analysis and physical characteristics are reported in Table 1. Chemical analysis of cement and its loss of ignition were done according to EN 196-2. Oxides in cement were determined by XRF.

2.2. Preparation of samples and curing

Seven different pastes were prepared from mechanically homogenized mixtures in three-dimensional rhythmically pulsing motion "TURBULA" mixer for 30 min. The mixtures include 1 control sample of pure PC, 2 binary and 4 ternary mixtures. Portland cement was partially replaced by BFS and MK with replacement levels of 0%, 10%, 20%, 30%, 40% and 50%. Maximum replacement level of PC by supplementary materials was 50 wt.% for all mixtures. Composition of binders is shown in Table 2.

Pastes prepared from binders were used for all measurements. Fresh pastes for the calorimetric measurement were prepared with water/binder ratio 1.2 and for hydration "in situ" water/binder ratio 0.6 was used. Powder samples for XRD, DTA and SEM analysis were prepared from hardened pastes (water/binder ratio 0.5) cured for 28 days at 25 °C and 95% rel. humidity. After 28 days samples were crushed and sieved and the hydration was stopped by washing the selected fraction with isopropyl alcohol and acetone. After drying in oven the samples were ground in a ball mill to required fineness.

Different water/binder ratio was used due to different volumes of dry mix. Water demand of dry mix is considerably higher in range of grams compared to range of tens or hundreds of grams.

Table 1
Chemical composition and physical characteristics of materials.

Parameters	Materials		
	PC (wt.%)	BFS (wt.%)	MK (wt.%)
SiO_2	20.04	37.44	56.8
TiO_2	–	0.24	0.5
Al_2O_3	4.07	7.54	37.84
Fe_2O_3	2.91	0.33	0.69
P_2O_5	–	0.03	0.07
MnO	–	0.37	0.005
MgO	1.98	10.62	0.4
CaO	65.96	40.94	0.69
Na_2O	0.12	0.49	0.17
K_2O	0.78	0.50	0.71
SO_3	3.04	1.47	0.02
Cl^-	0.05	–	0.01
LOI	3.27	0.19	1.88
Humidity	–	0.11	0.45
Density (g cm^{-3})	3.18	2.92	2.58
Spec. surface (m^2 kg^{-1})	345	414	2645

Table 2
Composition of binders.

	Materials		
	PC (wt.%)	BFS (wt.%)	MK (wt.%)
PC	100	–	–
PC/BFS 50/50	50	50	–
PC/BFS/MK 50/40/10	50	40	10
PC/BFS/MK 50/30/20	50	30	20
PC/BFS/MK 50/20/30	50	20	30
PC/BFS/MK 50/10/40	50	10	40
PC/MK 50/50	50	–	50

2.3. Methods

Calorimetric measurements of cement pastes were conducted on TAM Air isothermal calorimeter. The TAM AIR 8-Channel calorimeter consists of an eight channel calorimeter block and data logging system required for use with the TAM AIR thermostat. The calorimeters are twin-type (sample and reference), and designed for use with 20 ml glass or plastic ampoules or the 20 ml Admix ampoules. The mixtures of blended cements were placed in ampoules and lid. The water was injected in the ampoule using syringe. Five grams of sample and 6 ml of the water were used. The samples were gently stirred after adding of water and placed in the calorimeter. The measurement started few seconds after adding of the water. When heat is produced in a sample, isothermal calorimeter measures the heat flow. The sample is placed in an ampoule that is in contact with a heat flow sensor that is also in contact with a heat sink. When heat is produced or consumed by any process, a temperature gradient across the sensor is developed. This will generate a voltage, which is measured. The voltage is proportional to the heat flow across the sensor and to the rate of the process taking place in the sample ampoule. This signal is recorded continuously and in real time. For each sample there is a reference that is on a parallel heat flow sensor. During the time that the heat flow is monitored, any temperature fluctuations entering the instrument will influence both the sample and the reference sensors equally. This architecture allows a very accurate determination of heat that is produced or consumed by the sample alone while other non-sample heat disturbances are efficiently factored out.

Powder samples prepared from hardened cement pastes cured for 1 month were tested on X-ray diffractometer Empyrean. X-ray diffraction analyzer is equipped with 2D fast detector and Cu-anode ($\lambda_{K\alpha1}$ = 0.15418 nm, $\lambda_{K\alpha2}$ = 0.15418 - nm) and automatic motorized divergence slits at convention Bragg–Brentano parafocussing Θ–Θ reflection geometry, scan range 5–90 2Θ, scan step size 0.0131303. Data were processed using High Score Plus software.

The in situ X-ray diffraction analyses were conducted on Bruker D8 Advance diffractometer equipped with Cu-anode ($\lambda_{K\alpha}$ = 0.15418 nm), 1-D position sensitive detector and variable divergence slits at convention Bragg–Brentano parafocussing Θ–Θ reflection geometry. Step size – 0.04° 2θ, time per step – 188 s. The duration of individual scans was approximately 20 min, time of the whole experiment was 24 (PC) and 36 h (PC/BFS 50/50, PC/BFS/MK 50/20/30, PC/MK 50/50) respectively. The measured data were processed using Diffrac plus software. For the XRD the sample with the standard was mixed with water (w/c = 0.6). The paste was placed in a sample holder and covered with kapton foil to prevent carbonation.