Construction and Building Materials 148 (2017) 411–418

Contents lists available at ScienceDirect

Construction and Building Materials

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

Rational design of cement composites containing pozzolanic additions

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HIGHLIGHTS

- New approach to dosing of pozzolanic additions in concrete based on the phase composition of pozzolana was proposed.
- Waste ceramics can be effective cement substitute if its composition is taken into account.
- Behavior of the amorphous portion of waste ceramics is comparable to metakaolin.

ARTICLE INFO

Article history:
Received 20 May 2016
Received in revised form 24 April 2017
Accepted 5 May 2017
Available online 13 May 2017

Keywords:
Cement composites
Pozzolanic additions
XRD analysis
Solid state NMR spectroscopy
Mechanical properties
Freeze/thaw resistance

ABSTRACT

In cement composite design, pozzolanic additions (PAs) are primarily considered as mass equivalents of cement to be replaced. This paper presents a modification to the traditional approach that takes into account the amounts of active and passive components in a particular PA. The practical application of the modified design method is demonstrated for a red-ceramic residue from brick production. First, the residue is physically and chemically characterized via particle size distribution analysis, X-ray fluorescence spectroscopy, the Chapelle test of pozzolanic activity, and quantitative X-ray diffraction analysis to obtain detailed information on its activity. Subsequently, the effective pozzolanic properties of the residue are assessed by investigating the lime hydrate-ceramic system using solid-state magic angle spinning ^{27}Al and ^{29}Si nuclear magnetic resonance spectroscopy analysis and compressive strength measurements. Finally, cement composites containing different dosages of the ceramic residue are designed using the modified approach and their mechanical and durability properties are compared with reference samples prepared via the conventional method. The experimental results show an improvement of up to 35% in compressive strength and a significant gain in freeze/thaw resistance using the proposed approach.

1. Introduction

Pozzolanic additions (PAs) of various types and origins became common components of cement composite design in recent decades. PAs contribute to the hydration process of cementitious materials, influencing the nature of the hydration products and, consequently, the durability of the final composites [1]. Other possible benefits of PA application are lower energy consumption, lower CO_2 production related to concrete production [2], and the possibility of lower production costs for blended cements. However, the effectiveness of the application of various PAs to partially replace cement depends on their chemical and physical properties. The most important parameter affecting the quality of PA is the content of amorphous phases because only the amorphous part participates in the hydration reactions; the crystalline minerals constitute a passive component, i.e., filler. Despite this well known fact, in cement composite design, PAs are typically considered as mass equivalents of cement to be replaced, which sometimes leads to worse-than-expected results, particularly for the mechanical parameters, as observed e.g. for fly ash and zeolite additions [3,4].

The design of PA-containing cement composite mixtures can be improved significantly by taking the amounts of active and passive components in the PA into account. One important indicator of a PA's appropriate performance in blended cements is the pozzolanic activity, which can be measured by various methods [5]. In addition to the fineness, which influences the pozzolanic reaction rate, the pozzolanic properties of a PA depend

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http://dx.doi.org/10.1016/j.conbuildmat.2017.05.032
0950-0618/

on the content of species able to react with $Ca(OH)_2$. These species are either (and more frequently) amorphous (glassy) or crystalline (e.g. larnite β-$CaSiO_4$, which is present in some types of blast furnace slag). The elementary composition of a PA is its most frequently published characteristic, but it does not provide much information on the real reactivity of a material. Typical oxide composition, content of amorphous matter and pozzolanic activity expressed by means of Chapelle test of the most common PAs are provided in Table 1.

Thermally treated clays, i.e., ceramics or just dehydroxylated (non-sintered) clay minerals, were recognized as pozzolanic materials in Ancient Rome, where they were frequently used as hydraulic additives to lime mortars [23]. Recently, calcined clays – in form of ceramic or metakaolin – have been a popular focus regarding the role of pozzolanic admixtures for concrete production [20,24–27]. However, the results of mechanical properties have frequently been unconvincing when the ceramic powder was used. The 28-day compressive strengths of cement composites with 20% ceramic content have been found to be 7–32% lower than those for reference mixtures by several research groups [20–22,28]. On the other hand the results obtained with various kinds of metakaolin have been positive – at least some kinds of metakaolin are able to substitute OPC adequately [19,29]. Therefore, the appropriate design of cementitious composites containing ceramics as partial cement substitutes remains challenging.

In this paper, we present a cement composite design approach that can overcome some of the current difficulties related to the application of PA in blended cements. In the traditional approach to cement composite design, a PA is considered as a fully adequate cement substitute; however, this is not true for most PAs. As follows from Table 1, most of PAs contain certain portion of crystalline minerals which are not taking part in pozzolanic reaction and act just as filler. Therefore, knowing – and considering – the amount of active substances in the applied PA is crucial for appropriate PA-containing composite design. The practical applicability of the modified design method is demonstrated for a red-ceramic residue, which faces similar problems – insufficient mechanical properties – when it is used as Portland cement substitute. Firstly the PA was characterized and its ability to react with $Ca(OH)_2$ was tested. Secondly the concrete containing studied PA was prepared in a conventional way and modified way ant their properties were compared.

2. Experimental details

The ceramic grinding dust (CGD) is generated as industrial waste in a modern facility in the Czech Republic that produces vertically perforated ceramic blocks. The chemical composition of the CGD was examined via X-ray fluorescence spectroscopy (XRF) using a Thermo ARL 9400 XP instrument. The obtained data were evaluated using Uniquant 4 software. The particle size distribution was determined using a laser diffraction analyzer (Fritsch, Analysette 22 MicroTec plus). The conventional grading curve was obtained using a standard sieve set [30]. The Blaine specific surface area was measured according to [31]. The pozzolanic activity was characterized by the Chapelle test [32]; the amount of fixed $Ca(OH)_2$ was determined after 1, 3 and 7 days of reaction. The density of the raw materials used was determined via helium pycnometry (Pycnomatic ATC). The pH of the CGD was measured in its water leachate (L/S = 10). The SEM image of CGD was acquired by help of JEOL JSM 6510 SEM. The phase composition was studied via X-ray diffraction (XRD) using a PANalytical X'Pert PRO system. The present phases were identified by help of PDF-2 database. Quantification of present phases was achieved using Rietveld analysis (Topas code) with an internal standard (10% of zincite ZnO was added to the sample).

The CGD-$Ca(OH)_2$ system was studied using CL 90 S lime hydrate. The pastes were prepared with CGD contents ranging from 0 to 90%, and the amount of water was varied to obtain a constant consistency (160-mm spill according to the standard ČSN EN 1015-3 [33]). The demolded paste specimens (160 × 40 × 40 mm) were stored under laboratory conditions and continuously wetted by water spraying. The compressive strengths of pastes were measured after 28 days and 6 months of curing using the standard ČSN EN 1015-11 method [34]. Simultaneous TG/DSC analysis of the hardened CGD-lime pastes was conducted with a Setaram calorimeter Labsys Evo under inert atmosphere between room temperature and 1000 °C. The TG/DSC specimens were conditioned at 50 °C for 12 h to partially remove the physically bound water. The solid-state MAS NMR spectroscopy analysis was performed at 11.7 T using a Bruker AVANCE III HD 500 WB/US NMR spectrometer. The ^{27}Al MAS NMR spectra were acquired at a spinning frequency of 11 kHz, a Larmor frequency of 130.287 MHz and a recycle delay of 2 s, and the spectra were referenced to the external standard $Al(NO_3)_3$ (0 ppm). The number of scans for the acquisition

Table 1
Typical parameters of Pozzolanic additions.

Pozzolanic addition	Oxide composition	Amorphous content	Chapelle test	Reference
	% wt.	% wt.	mg $Ca(OH)_2$/g	
Silica fume	~100% SiO_2	>90	1438	[6,7]
Class F fly ash	50–60% SiO_2 20–30% Al_2O_3 4–10% Fe_2O_3 1–10% CaO	77–86	660	[6,8–11]
Rice husk ash	>80% SiO_2	Highly variable	600–1140	[7,11–13]
Volcanic glass	64–68% SiO_2 13% Al_2O_3 7% Fe_2O_3	57–71	140–460	[14]
Zeolite (heulandite II)	67% SiO_2 13% Al_2O_3 3% CaO	N/A	555	[15]
Metakaolin	47–54% SiO_2 30–47% Al_2O_3	High	700–2080	[16–19]
Red clay ceramic	52–67% SiO_2 14–19% Al_2O_3 5–7% Fe_2O_3 2–6% CaO	N/A	N/A	[20–22]