Cement & Concrete Composites 45 (2014) 136–147

Contents lists available at ScienceDirect

Cement & Concrete Composites

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

High-volume natural volcanic pozzolan and limestone powder as partial replacements for portland cement in self-compacting and sustainable concrete

K. Celik [a], M.D. Jackson [a], M. Mancio [a,1], C. Meral [a,2], A.-H. Emwas [b], P.K. Mehta [a], P.J.M. Monteiro [a,*]

[a] *Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA*
[b] *King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia*

ARTICLE INFO

Article history:
Received 1 October 2012
Received in revised form 3 August 2013
Accepted 10 September 2013
Available online 18 September 2013

Keywords:
Basaltic ash pozzolan
Limestone filler
Self-consolidating concrete
Compressive strength
Chloride migration
Petrographic analysis

ABSTRACT

A laboratory study demonstrates that high volume, 45% by mass replacement of portland cement (OPC) with 30% finely-ground basaltic ash from Saudi Arabia (NP) and 15% limestone powder (LS) produces concrete with good workability, high 28-day compressive strength (39 MPa), excellent one year strength (57 MPa), and very high resistance to chloride penetration. Conventional OPC is produced by intergrinding 95% portland clinker and 5% gypsum, and its clinker factor (CF) thus equals 0.95. With 30% NP and 15% LS portland clinker replacement, the CF of the blended ternary PC equals 0.52 so that 48% CO_2 emissions could be avoided, while enhancing strength development and durability in the resulting self-compacting concrete (SCC). Petrographic and scanning electron microscopy (SEM) investigations of the crushed NP and finely-ground NP in the concretes provide new insights into the heterogeneous fine-scale cementitious hydration products associated with basaltic ash-portland cement reactions.

1. Introduction

Portland cement concrete is the most widely used human-made commodity on the planet; about 25 billion metric tonnes are produced globally each year [1]. About 3.3 billion tonnes of portland cement (OPC) were used in 2010 [2], mainly for concrete construction projects. Concrete domination in construction environments results from its proven flexibility and adaptability, low maintenance requirements during the service life of most structures, and widespread availability of its raw constituents [3]. However, the massive production and consumption cycle of concrete has significant environmental impacts [4]. Global portland cement production currently accounts for 7% (2.1×10^9 tonnes) of anthropogenic carbon dioxide (CO_2) emissions annually, resulting mainly from production of cement clinker, the active binding ingredient of concrete [5]. Because kiln-fired portland cement is an energy-intensive material, requiring 4–5 GJ per ton of cement [4], about half of these emissions occur through combustion of fossil fuels. The remaining emissions result from calcination of limestone: one kg of portland cement clinker releases 0.87 kg of CO_2 to the atmosphere [6]. Increased volume fractions of supplementary cementitious materials (SCM), such as fly ash, slag, and volcanic pozzolans produce more environmentally-sustainable concretes, and also yield mixtures with high workability, ultimate strength, and durability [3].

To eliminate 1 billion tonnes of CO_2 per year through the concrete sector, approximately 50% of the clinker factor (CF) of portland cement must be replaced with materials produced with very low carbon dioxide emissions [7]. This would require 1.58 billion tonnes of alternative SCM annually. High volume fly ash (HVFA) mixtures have been utilized successfully in many projects as a low-cost alternative to conventional portland cement concrete, with proven technical and environmental advantages [8]. However, the global availability of fly ash is about 800 million tonnes annually [9], and not all of it is suitable for use in blended cements, or in concrete mixtures. Recently, natural basaltic ash pozzolan replacement of portland cement at 25 mass%, from Saudi Arabia, has been shown to be a successful alternative [10]. In addition, natural zeolite and volcanic tuff pozzolan replacement of OPC at 50 mass%, from Turkey, and a higher w/c ratio than the present study led to a slow strength gain, but relatively good compressive strength and durability characteristics [11]. Studies of portland cement-based

---

* Corresponding author. Tel.: +1 510 643 8251; fax: +1 510 643 5264.
E-mail addresses: kcelik@berkeley.edu, ckemal@gmail.com (K. Celik), mdjackson@berkeley.edu, mdjjackson@gmail.com (M.D. Jackson), mancio@gmail.com (M. Mancio), caglameral@gmail.com (C. Meral), abdelhamid.emwas@kaust.edu.sa (A.-H. Emwas), pkmehta@berkeley.edu (P.K. Mehta), monteiro@ce.berkeley.edu (P.J.M. Monteiro).

[1] Present address: Unisinos University, Graduate Program in Civil Engineering (PPGEC), Av. Unisinos, 950, 93022-000 Sao Leopoldo, RS, Brazil.

[2] Present address: Department of Civil Engineering, Middle East Technical University, 06800 Ankara, Turkey.

0958-9465/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.cemconcomp.2013.09.003

ternary and quaternary blends containing combinations of fly ash, silica fume, blast furnace slag, limestone filler and natural volcanic pozzolans show that blended cements can be optimized to minimize the shortcomings of each component, resulting in synergistic cementitious systems [12,13].

This research investigates the mechanical and durability performance of SCC mixtures containing high volume portland cement replacements of finely-ground limestone (LS) and finely-ground basaltic ash (NP) from Harrat Rahat, Jabal Kadaha quarry, Medina Province, Saudi Arabia. Western Saudi Arabia has numerous lava and cinder cone fields in widespread *harrats* (Fig. 1 [14]), produced about 25 Ma ago through continental intraplate volcanism associated with rifting of North East Africa to form the Gulf of Aden and the Red Sea [15]. In the laboratory experiments, we utilize binary OPC-NP mixtures with finely ground 30 mass% and 50 mass% NP (30 NP, 50 NP), and ternary OPC–NP–LS mixtures with 30 NP, 40 NP, and 50NP with or without 15 mass% (15 LS). Although the overall pozzolanicity of the ash has been previously measured [16], the role of individual components has not been specifically evaluated. Here, the crushed cinders are described with petrographic analyses (Fig. 2) to show how an inexpensive, straightforward optical microscopic technique can provide rapid insights into the reactivity of the various components of typical basaltic volcanic ash – volcanic glass, crystal fragments, lava rock fragments, and vesicle surface coatings – and the new cementitious products formed in the resulting concrete. Construction material testing applications then describe the mechanical properties and durability performance of the various blends, and the influence of the LS and NP mixtures in the ternary OPC blends on the strength and durability properties of the concretes is discussed. Petrographic and scanning electron microscopy (SEM) investigations of the 70 OPC–30 NP and 50 OPC–50 NP binary blends provide an initial evaluation of the results of the testing experiments and how compositions of cementitious hydrates vary as a function of pozzolanic reaction of NP components with OPC.

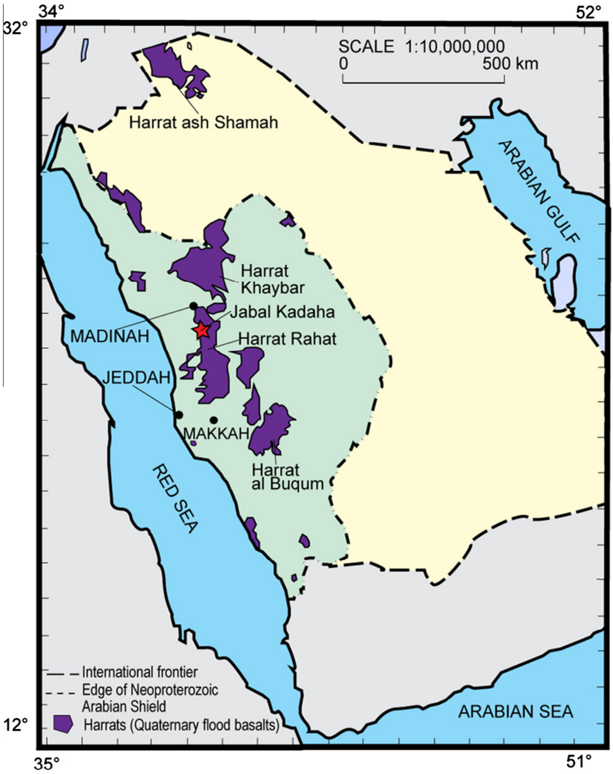

Fig. 1. Schematic map showing the cenozoic lava and cinder cone fields, or *harrats*, of western Saudi Arabia, adapted from [15], and the site of the basaltic ash from Jabal Kadaha, Harrat Rahat used in the experimental concretes.

2. Materials

2.1. Geologic materials used as portland cement replacements

2.1.1. Limestone powder

During the last decade, LS as calcite, or crystalline $CaCO_3$, has proven to be an effective partial replacement for OPC [17]. LS has two functions: it acts as a relatively inert calcareous filler and a limited participant in the hydration process [18–20]. During cement hydration, finely ground $CaCO_3$ reacts with C_3A and C_4AF to form high and low forms of carboaluminates [21]. Calcium hemicarboaluminate forms as an early hydration product in calcite-containing OPC, and then converts nearly completely to calcium monocarboaluminate, a stable AFm phase, after about 28 days [22]. The particle size of LS must be considered in the mix design because the early strength of the concrete depends on blended cement composition and LS fineness, since interaction between gypsum and limestone during early C_3A hydration interferes with setting time [23]. An acceleration of C_3S hydration may occur at early ages when LS is interground with clinker [24]. The catalytic effect results from the high specific surface area of LS, which produces nucleation sites for cement hydration products such as calcium carbosilicate hydrate [25], thus reducing the size of C–S–H agglomerations. In blended cements with up to 5% calcite, for example, almost all of the added calcite reacts with cement [18]. The resulting concretes show compressive strength [26], flexural strength, and drying shrinkage [27] similar to control concretes without LS. At 25% sand mass replacement with LS in mortar specimens, the fine $CaCO_3$ particles produce denser packing of the cement paste and better dispersion of cement grains [28]. When LS replacement of OPC exceeds 15% by mass, however, the less reactive calcite has a dilution effect on the more reactive cement; the amount of cement paste is considerably reduced, resulting in lower compressive strengths and physical modifications [25,29]. Durability decreases as water absorption and chloride diffusion coefficients increase [29].

2.1.2. Basaltic volcanic ash

Volcanic ash pozzolans fall into two major categories: cinder cone eruptions produce scoriae, frothy droplets of molten rock with mainly basaltic compositions, where amorphous glass is usually the predominant reactive component, while more explosive pyroclastic flow eruptions of molten and solid rock fragments produce complex deposits that commonly develop secondary pozzolanic clay and zeolitic surface coatings through interactions with interstitial ground and surface waters [30–33]. The binding pozzolanic mortars of 2000-year-old concretes in the monuments of imperial age Rome, for example, contain 40–50 vol.% scoriaceous volcanic ash from a specific pyroclastic flow with reactive zeolitic and clay mineral surface coatings [33]. Recently, basaltic ash erupted from cinder cones in Saudi Arabia has been used successfully as SCM that complies with the requirements of ASTM C618 for Class N natural pozzolan [14,16,34]. Moufti et al. [16] found that the pozzolanic reactivity of lime with finely-ground cinders from Harrat Khaybar, passing the #200 sieve, satisfies the Italian standard. Khan and Alhozaimy [10] found good effectiveness for up to 25% OPC replacement [16]. The effectiveness of the ash as a larger volume 30–50 mass% OPC replacement has not been evaluated, however, and the reactive components of the ash and associated cementitious products in the resulting concretes have not been described in detail.