Construction and Building Materials 102 (2016) 631–639

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effect of alkali content of cement on properties of high performance cementitious mortar

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HIGHLIGHTS

- Impact of cement alkali content on properties of very low w/c HPCM was studied.
- Higher alkali level negatively affects workability, setting and strength of HPCM.
- Higher alkali level increased shrinkage, permeable voids and RCP in HPCM.
- Even in HPCMs with very low w/c, ASR was observed when a reactive aggregate was used.
- Fly ash was effective in mitigating ASR in HPCMs.

ARTICLE INFO

Article history:
Received 25 January 2015
Received in revised form 15 September 2015
Accepted 17 October 2015
Available online 13 November 2015

Keywords:
HPCM
UHPC
Alkali content
Fresh property
Compressive strength
Alkali–silica reaction
Flexural strength loss

ABSTRACT

The use of very low water-to-binder ratio (w/b) in high-performance cementitious mixtures (HPCM) such as ultra-high performance concrete (UHPC) is gaining popularity. Typically these mixtures consist of Portland cement, pozzolans, water, aggregate, chemical admixtures and steel fiber. The properties of such mixtures including workability, strength, dimensional stability and durability are sensitive to the quality and the proportions of the materials used. In particular, due to high cementitious materials content and low w/b ratio of these mixtures, the alkali content of Portland cement can have a significant effect on the fresh and hardened properties. However, there is limited information available in the literature on the influence of cement alkalinity on the properties of these mixtures. In order to have a closer examination of the influence of alkali content of cement on the properties of such mixtures, a series of Portland cement mortars having a w/c ratio of 0.20 and a range of cement alkali contents were evaluated in this study. The workability, setting time, compressive strength, drying shrinkage, rapid chloride ion penetration, volume of permeable voids and alkali–silica reaction potential of HPCM using reactive aggregate were studied as a function of the alkali content of cement ranging from 0.49% to 0.88% Na_2O_{eq}. The test results showed that when the alkali content of cement was higher than 0.70%, the workability of HPCMs decreased significantly as the alkali content increased. An increase in the alkali content of cement delayed the time of final setting, reduced the compressive strength, and increased the rapid chloride ion permeability, drying shrinkage and volume of permeable voids of HPCM. As the alkali content of cement increased, rapid and significant expansion due to ASR was observed in HPCM, along with significant loss in flexural strength of test specimens, even though the w/c was maintained at 0.20. Identical set of tests were conducted on parallel HPCM specimens containing Class F fly ash as a cement replacement material, and significant differences in results were observed when compared with pure Portland cement mixtures.

1. Introduction

Ultra-high performance concrete (UHPC) typically refers to cementitious mixture having compressive strength higher than 150 MPa at the age of 28 days [1–4]. The development of UHPC using local materials is increasingly gaining attraction as the benefits of using UHPC are being recognized [3,5,6]. However, this approach is challenged by the limited availability of high quality materials in many regions. Typically, UHPC is characterized by the use of siliceous aggregates, high cement contents (often >1000 kg/m^3) and water-to-cementitious materials (w/cm) ratio less than 0.2 to achieve the desired properties [3–6]. When high alkali content cement is used to produce UHPC, an ideal scenario can exist for potential alkali–silica reaction (ASR) to occur

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http://dx.doi.org/10.1016/j.conbuildmat.2015.10.110
0950-0618/

particularly if the available aggregate is reactive. This situation can also exist when low alkali content cement is employed as the cement content of the mixture is typically high, and the total alkali content of concrete can be excessive. For conventional concrete the total alkali content of cement is typically restricted to less than 3 kg/m^3 as a preventive measure for ASR distress [7]. The alkali content of the cement can also be a sensitive factor in affecting the fresh and the hardened properties of concrete [8–11]. However, previous studies on the effect of cement alkalinity on the properties of concrete were conducted primarily on conventional concrete. The available literature on the properties of UHPC affected by cement alkalinity is still limited.

For conventional concrete, it is generally admitted that there is an important effect of the alkali content of cement on the ASR induced expansion. When alkali content of cement increases, or total alkali content of concrete increases, the potential for ASR in concrete increases [11–13]. A study on the ASR induced expansion of concrete with alkali content of cement varying from 0.9% to 1.25% Na_2O_{eq} was conducted by Rogers et al. [12]. The base Portland cement had alkali content of 0.9% Na_2O_{eq}, and higher alkali content was achieved by dissolving corresponding quantity of sodium hydroxide (NaOH) into mixing water. The test results showed an approximately linear relation between increasing ASR expansion and increasing alkali content [12]. In another study, 70–80% of the expansion was reduced when the alkali content of mortar mixtures was reduced from the higher (13.4 kg/m^3) to the lower value (6.2 kg/m^3) [11].

Besides ASR, alkali content of cement has impact on the fresh properties of normal concrete [8–10,14–19]. In the past studies, a decrease in the workability of fresh cementitious mixtures was observed with an increase in the alkali content of cement [8,10,14]. This phenomenon was explained by the mechanism that the increased alkali cations in the liquid phase of fresh cementitious mixture accelerated the hydration of C_3A by depressing the Ca^{2+} cations released from gypsum whose effectiveness was therefore decreased [8,15–17]. An increase in alkali content was also observed to cause accelerated hydration of cement and promoted setting [8,9,18,19].

Alkali content of cement also has impact on the compressive strength of normal concrete [8–10,20–25]. Past studies have shown that increasing alkali content reduced the compressive strength of concrete [8–10,20–25]. This behavior was attributed to the porous microstructure and lower strength of the alkali-containing C–S–H gel of hardened mixture developed in presence of the high alkali condition [8–10,20–25].

The present study was carried out to investigate the effect of alkali content of cement on the properties of the Portland cement mortar fraction of UHPC. Such Portland cement mortar had 28-day compressive strength around 110 MPa, which is referred to as high performance cementitious mortars (HPCM). It was successfully used to develop UHPC by simply adding silica fume and steel fiber [5,6]. In order to isolate the impact of alkali content of the cement on the properties of HPCM and avoid any variability resulting from other factors such as differences in the chemical composition of the cement and fineness, a cement having an alkali content of 0.49% Na_2O_{eq} was used as a reference cement. Using the reference cement, a series of HPCMs with increasing alkali content were produced, wherein the alkali content of the cement was adjusted by adding reagent grade sodium hydroxide to the mix water. This was done to simulate HPCMs produced using higher alkali cements. The practice of adding reagent grade sodium hydroxide to a reference cement to elevate its alkali level is a commonly employed procedure in standard test methods and research studies investigating alkali content affected properties of concrete [20–22,24–26]. The properties of HPCM investigated include workability, setting time, compressive strength, drying shrinkage, rapid chloride ion penetration (RCP), volume of permeable voids, expansion and flexural strength loss due to ASR. Fly ash (FA) was also used in some of the HPCM formulations to understand the behavior of FA under various alkali contents of cement.

2. Experimental program

2.1. Materials

In the experimental study, a Type III Portland cement meeting ASTM C150 specification was used. The specific gravity, Blaine's surface area and the alkali content of the cement were 3.15, 540 m^2/kg and 0.49% Na_2O_{eq}, respectively. In specific mixtures, a class F fly ash was used as a cement replacement material on a mass basis. The specific gravity of fly ash was 2.26. Table 1 lists the chemical properties of cement and fly ash.

The fine aggregate used in this study was a reactive sand (containing volcanic glass) meeting the ASTM C33 gradation specification. The gradation of the fine aggregate is shown in Table 2. The specific gravity, water absorption, and fineness modulus of the fine aggregate were 2.58, 1.5%, and 2.93 respectively.

Reagent-grade sodium hydroxide (NaOH) in pellet form was used to increase the alkali content of the cement. In this study, Melflux® 4930F, a powder form of polycarboxylate ether-based high-range water-reducing admixture (HRWRA) was used to improve the workability of HPCM.

2.2. Mixture proportions

A total of 9 HPCM mixtures were investigated to study the effect of alkali content of the cement on the properties of HPCM, with and without FA. The w/cm and the fine aggregate-cement mass ratio were fixed at 0.2 and 1.25, respectively, throughout the study. In mixtures with FA, a dosage of 17% by mass of the cementitious material was used. The alkali content of the mixtures was adjusted by adding reagent grade NaOH to the mixing water to achieve different alkali levels of 0.49%, 0.60%, 0.70%, 0.75%, and 0.88% Na_2O_{eq} by mass of cement. The mixture proportions of the 9 HPCMs are shown in Table 3.

As Table 3 shows, the first five HPCM mixtures C, A1, A2, A3 and A4 had the same mixture proportions except that the alkali content was varied from 0.49% to 0.88% Na_2O_{eq} by mass of cement. The dosages of HRWRA were kept constant at 0.75% by mass of cementitious materials. The effect of alkali content on the workability, time of setting, compressive strength and drying shrinkage of HPCMs without FA was determined by comparing these HPCMs.

The next two HPCM mixtures A3a and A4a were prepared by increasing the dosage of HRWRA of HPCMs A3 and A4 to 1% and 1.5%, respectively, to match the workability of other mixtures, i.e. HPCMs C, A1 and A2 (see Table 4). In this case, the influence of compatibility on other properties is minimized. The effect of alkali content on the ASR induced expansion and the associated loss in flexural strength of HPCMs without FA was determined by comparing HPCMs C, A1, A2, A3a, and A4a.

The last two HPCMs CF and A4F were prepared by replacing 17% of the cement with FA in HPCMs C and A4, respectively, while maintaining a constant dosage of HRWRA at 0.75%. HPCMs C, A4a, CF and A4F all exhibited similar workability (see Table 4). The effect of alkali content on the workability, setting time, compressive strength and drying shrinkage of HPCMs with FA was determined by comparing HPCMs C, A4, CF and A4F. The effect of alkali content on the ASR induced expansion and associated loss in flexural strength of HPCMs with FA was determined by comparing the performance of HPCMs C, A4a, CF and A4F.

The quantities of materials used for 1 m^3 HPCM are presented in Table 4.

2.3. Specimens preparation

Fresh HPCM mixtures were prepared by a UNIVEX M20 planetary mixer. For each HPCM mixture, the corresponding amount of NaOH was dissolved into the mixing water before use. At first, the cementitious materials, fine aggregate, and the HRWRA were dry mixed for 1 min at low speed (100 RPM). Then the mixing water or NaOH solution was added to the dry mixture. The mixing continued at low speed for 3–4 min before the mixture became flowable. Finally, the flowable

Table 1
Physical and chemical properties of materials.

Materials name	Type III cement	Fly ash
LOI (%)	1.34	0.60
SiO_2 (%)	20.4	54.1
Fe_2O_3 (%)	3.5	8.0
Al_2O_3 (%)	5.0	27.8
CaO (%)	64.4	1.3
MgO (%)	1.0	0.9
Na_2O_{eq} (%)	0.49	2.13
SO_3 (%)	3.5	0.16