Cement & Concrete Composites 32 (2010) 603–610

Contents lists available at ScienceDirect

Cement & Concrete Composites

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

Effect of curing temperature on the nonevaporable water in portland cement blended with geothermal silica waste

Lauren Y. Gómez-Zamorano [a,*], José I. Escalante-García [a,b]

[a] Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, 66451, San Nicolás de los Garza, Nuevo León, Mexico
[b] Centro de Investigación y de Estudios Avanzados del IPN (Cinvestav – Unidad Saltillo), Carretera Saltillo-Monterrey, km. 13, Saltillo, Mexico

ARTICLE INFO

Article history:
Received 23 May 2007
Received in revised form 29 June 2010
Accepted 8 July 2010
Available online 13 July 2010

Keywords:
Curing temperature
Blended cement
Pozzolana
Nonevaporable water
Geothermal silica waste

ABSTRACT

This paper reports the results of the utilization of a silica waste from a geothermal power generation plant as partial replacement of portland cement. To evaluate the reactivity of the silica waste, the effect of the curing temperature was analyzed by means of the estimation of nonevaporable water (NEW) and calcium hydroxide (CH) contents. Pastes of portland cement substituted with 0%, 5%, 10% and 15% of geothermal silica waste (GSW) and water/solid ratio of 0.50 were cured at 10, 20, 40 and 60 °C for up to 540 days. The pastes were characterized by thermogravimetric analysis. According with the CH estimations, the geothermal silica showed a strong pozzolanic behavior. Nevertheless, the NEW contents were lower compared to those of neat cement, in agreement with other reports. The results of NEW contents of neat and blended cements were processed to obtain a modified NEW (mNEW) that excluded the water corresponding to the CH. The mNEW data indicated that the blended cements reached higher contents of nonevaporable water.

1. Introduction

The use of replacement materials for ordinary portland cement (OPC) is a practice that has increased considerably due to advantages in the savings of natural resources, energy and CO_2 emissions, as well as in the improvements in the properties of the cementitious materials. This highlights the importance of searching for new potential wastes or by products as replacements or additives to portland cement. One potential waste is that obtained in geothermal power plants, as part of the process of energy production by means of steam extraction from the underground. Such geothermal silica waste (GSW) is obtained as a mixture of geothermal brine and steam (naturally pressurized) that undergoes a series of changes during heat extraction. As its temperature is reduced (from about 200 °C) a solid precipitates from the mixture. The silica waste used in this work was obtained from the geothermal Cerro Prieto plant in Mexico, which generates up to 50 thousand tons of it yearly. The general characteristics of this material were published elsewhere [1] and are summarized as follows: the chemical composition is rich in SiO_2, with NaCl and KCl and potassium chlorides; it is a white predominantly amorphous powder with nanometric particle size of about 100 nm and its density is of 2.1 g/cm^3. There is little information about the use of geothermal silica waste in portland cement based materials and, in view of the similarities with silica fume (SF), it was expected that the former would show pozzolanic character and also would present similar effects on the cement hydration with regards to nonevaporable water (NEW) contents.

Several authors [2–9] have described the effects of SF on the chemically bonded water produced by OPC with different replacement levels and water/solid (w/s) ratios: the amounts of NEW for neat cements were higher than those in blended cements for a given w/s ratio, especially at long periods of hydration. Moreover, the greater the silica load, the lower the NEW relative to the neat cement values. These observations were reported with evidence of pozzolanic behavior of the SF. The reduced NEW values were explained in the literature in several ways. Zhang and Gjørv [4] attributed the NEW reduction to the increased average chain length of polysilicates in the C–S–H gel, with both SF content and time, which was believed to result in the release of water, hence lower NEW values. Attlasi [2] concluded that the water from CH involved in the pozzolanic reaction is released as evaporable water, lowering the total amount of NEW per hydrated cement content in SF blends. Also, the lower NEW values of pastes with SF (mentioned above) can be explained by postulating that, at high SF contents, the availability of water for silicate hydration is severely restricted by the impermeability of the paste that resulted after the refinement of the microstructure [10]. Yogendran et al. [5] pointed out that since the pozzolanic reaction reduces the CH amounts in OPC blended with SF, and the cement fraction is lower, the NEW values are reduced and it is not possible to directly

---

* Corresponding author. Tel.: +52 81 14920378; fax: +52 81 10523321.
E-mail address: lauren.gomezzm@uanl.edu.mx (L.Y. Gómez-Zamorano).

0958-9465/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2010.07.004

compare NEW values of a neat and the blended cement; after a direct comparison of NEW values excluding CH water losses, the NEW values in the blended cements were higher than those of the neat cements due to the pozzolanic reaction and the accelerating effect on the cement hydration in spite of the lower neat cement fraction. Sellevold and Justnes [8] reported that the SF reacts directly with the CH to produce C–S–H binding no additional water.

In the same context, but using fly ash and volcanic ash, Escalante-García [11] reported NEW values from the replacement materials (NEW_R) based on a mathematical estimation from the correlation between the degree of hydration and the NEW total values. The results suggested that the hydration products of the pozzolanic reaction had a smaller water intake other than that from the CH; moreover, the NEW total values were enhanced in the presence of the pozzolan as due to enhanced hydration of the cement fraction. Escalante-Garcia et al. [12] also investigated the effect of the curing temperature of 20 and 60 °C in fluorgypsum binders with portland cement and fly ash additions, evaluating the reactivity. They reported that a fast formation of gypsum in the first days was evidenced by high NEW values.

The pozzolanic reaction consumes CH to form C–S–H; however the incorporation of additional water is uncertain. This opens the possibility for the formation of C–S–H (from various reactions) with different water contents, e.g. C–S–H from OPC calcium silicates and C–S–H from the pozzolanic reaction. Such factors make it difficult to directly compare NEW among neat and blended cements. A direct comparison between NEW values that excluded CH water losses is more suitable, comparing NEW only from the hydrates in both types of cements. Following from the above the main objective of this work was to analyze the NEW and CH contents from neat and blended cements, involving geothermal silica waste, cured under different conditions of temperature in order to understand fundamental aspects of the reactivity of the GSW and comparing the results with those reported by other authors [2–9].

2. Experimental procedures

2.1. Materials

Pastes were prepared using an ordinary portland cement (OPC) produced by Holcim-Apasco with slag and calcite additions, a geothermal silica waste from Federal Commission of Electricity (Cerro Prieto Plant, Mexico), Rheobuild 1000 superplastizicer (SP) and distilled water. The GSW had to be treated in order to eliminate the chlorides present by washing repeatedly with water at 80 °C, as described elsewhere [1]. Table 1 presents the chemical composition of the GSW and OPC.

Table 1
Oxide chemical composition of the silica waste and portland cement.

OXIDE	GSW	OPC
CaO	1.72	67.53
SiO_2	94.67	18.16
Al_2O_3	1.04	3.5
Fe_2O_3	–	2.52
MgO	0.53	1.89
Na_2O	0.66	0.89
K_2O	0.53	0.57
TiO_2	0.84	–
MnO	–	0.14
SO_3	–	4.05
Total	100	99.23

2.2. Pastes preparation and hydration

The OPC was replaced by GSW at (wt%) 0, 5, 10 and 15, using a w/s of 0.50. In order to avoid the agglomeration, due to the nanometric particle size of the GSW, the SP was used to obtain fluid pastes at (wt% relative to the cementitious material weight) 0.75, 1.0 and 1.25 for 5%, 10%, and 15% of GSW, respectively. Cubes of 5 cm were cast at a controlled temperature of 20 °C and maintained isothermally for 24 h for setting at 10, 20, 40 and 60 °C and relative humidity of 90%. The cubes were then demolded and submerged in plastic containers filled with $Ca(OH)_2$ saturated water at the same temperatures for curing up to 540 days.

2.3. Characterization

After the curing periods of 3, 7, 14, 28, 90, 180, 360 and 540 days, samples were obtained from the core of the cubes, ground and dried in a vacuum oven at 105 °C during 24 h. Hereafter, the fragments were further ground in agate containers in a planetary ball mill to pass a 106 μm mesh; the powders were used for further characterization. Loss on ignition measurements allowed estimation of estimate NEW by heating the hydrated samples at 120 °C for 1 h and then ignited at 950 °C for 1 h; the weight difference was referred to the ignited weight. The CH contents were graphically estimated by TGA from the weight loss step between 425 and 550 °C, simultaneous C–S–H decomposition was considered by graphical correction. The results were reported relative to the ignited weight at 900 °C.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 presents the results of evolution of CH concentration vs. time as measured by TGA for all cements. Since the presence of GSW dilutes the amount of OPC, the results for all blended cements were normalized as 100% OPC; e.g. at any given time the CH concentration for a blend with 10% GSW was increased to assume 100% OPC.

Fig. 1A shows the CH contents for the neat cement, which reached above 10% after 3 days. At the initial stages, higher curing temperatures resulted in higher rates of CH production. The rates of CH generation were reduced drastically after 90 days for the higher temperatures (40 and 60 °C) and after 180 days for lower temperatures (10 and 20 °C); however, after 360 days the CH contents of specimens cured at all temperatures were fairly similar, indicating similar degrees of hydration. The maximum concentration of CH for the neat cement was relatively low (~16%) compared to those reported by other authors (~20%) [11,13]. This could be attributed to the mineral admixtures added to the cement in plant, which dilute the clinker content; thermal and quantitative X-ray diffraction analyses allowed to estimate ~10% $CaCO_3$ and ~5% of blast furnace slag. The reported ~16% CH already considers the presence of $CaCO_3$; however, if the CH content is corrected for the presence of the slag, the value would increase to ~16.8%. However, since the slag reacts with CH [14,15], an additional 1–2% of CH could be added assuming it reacted with the slag. Thus the total equivalent CH content would be at ~19%, close to the normally reported values for fully hydrated cements.

The observations regarding the estimated CH contents in the blended cements are summarized as follows.

3.1.1. Effect of replacement level

The concentrations of CH for blended cements were lower compared to the neat cement; the values increased for the first 7–