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Cement and Concrete Research 33 (2003) 1883–1888

CEMENT AND CONCRETE RESEARCH

Nonevaporable water from neat OPC and replacement materials in composite cements hydrated at different temperatures

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Received 19 November 2002; accepted 25 June 2003

Abstract

Pastes of two neat OPC and three blended cements using GGBFS (60%), PFA (30%) and a volcanic ash (23%), were cured for up to 1 year at five temperatures. The degree of hydration of the OPCs was estimated by quantitative X-ray diffraction analysis and by measurements of nonevaporable water by thermogravimetry. A correlation between the results from these techniques is presented for the neat OPCSs. The correlation was used to estimate the contribution to the nonevaporable water from the cement replacement material fraction for the blended cements. According to the estimated data, the slag displayed a hydraulic nature retaining significant amounts of water in its hydrates, the slag nonevaporable water values as function of time varied with temperature and the patterns were similar to those of degree of hydration of the neat cement. The data estimated for the two pozzolanic materials indicated that their hydrates retained small amounts of water in spite of the CH consumption.

Keywords: Hydration; Reaction; Temperature; X-ray diffraction; Thermal analysis; Blended cements

1. Introduction

The mineral admixtures used in blended cements can have pozzolanic or latent hydraulic reactive nature, they can modify the cement hydration and also contribute with cementitious products to the matrix structure [1]. The chemical composition of most of the pozzolanic materials show high Si and low Ca, the formation of additional cementitious products is via the well-known pozzolanic reaction; whether additional water, other than that provided by the CH, is required can be questioned. Due to its chemical composition, ground granulated blast furnace slag (GGBFS) also requires additional Ca to form C-S-H products [1–3]. The slag bears Ca and Si and it may also need additional water to form hydrates in a reaction similar to the pozzolanic reactions [4].

The temperature dependence of the hydration of the slag has been observed from techniques as isothermal conduction calorimetry [5,6] and by dissolving the reacted slag, measuring the unreacted slag [7–9]. The strength development of slag cements is slow at low temperatures and favored by high temperatures [10,11]. The pozzolanic reaction is also favored by increased hydration temperatures [1,12]. Studies on the reactivity of PFA at different temperatures were regarded by some authors [7] as not completely reliable.

The use of quantitative X-ray diffraction analysis (QXDA) to measure the degree of hydration (DOH) of cement phases has been reported for neat and blended cements [1,13,14] at various temperatures. The nonevaporable water (NEW) can also be used as a relative measure of the degree of hydration of the portland cement [15]; however, data regarding variations of the NEW at different hydration temperatures is not very common in the literature [16].

This work considers the relationship between DOH (by QXDA) and NEW (by thermogravimetry) for the neat cements. By correlating such results a predictive model was obtained to allow the estimation of NEW from the replacement materials fraction (in blended cements). Whether the formation of additional hydration products from the different replacement materials may demand additional water was evaluated based on the results obtained from such model. No literature report was found to separate the

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doi:10.1016/S0008-8846(03)00208-4

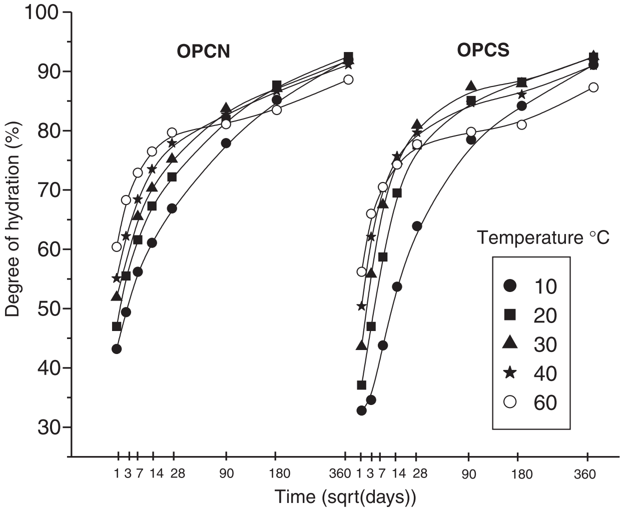

Fig. 1. Degree of hydration vs. time for the neat cements.

contributions to NEW from the cement and replacement material fractions.

2. Experimental

2.1. Materials

The materials and their chemical composition are published elsewhere, together with the initial hydration and curing procedures of the cement pastes [1,13]. Two OPCs named OPCN and OPCS were used to prepare three blended cements with ground granulated blast furnace slag (GGBFS), pulverized fuel ash (PFA) and volcanic ash (VA) as follows: 40% OPCN–60% GGBFS, 70% OPCN–30% PFA and OPCVA (77% OPCS–23% VA).

2.2. Characterization

After the selected curing periods representative samples were subtracted, hand ground and then dried for 24h in a vacuum desiccator. Samples for TGA (Stanton-Redcroft TGA760) were hand ground to pass a mesh of 125 μm before testing. Samples of ≈ 35 mg were ignited up to 900 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The NEW was considered as the losses in the range of 150–900 °C referred to the ignited weight. El-Jazari and Illston [17] found a peak at 176 °C ascribed to C-S-H dehydration using semi-isothermal DTG, Fordham and Smalley [18] used DTG and observed that such a peak at 176 °C overlapped one at 100 °C from the dehydration of pore water. Taylor [19] suggested that the volatiles retained at 150 °C correspond to the nonevaporable water, for experimental conditions such as 50 mg sample, heating rate of 10 °C/min and under 15 ml/min N_2 gas flow, in this work the smaller sample size compensates to some extent the higher heating rate used. The DOH used for the clinker phases were those previously reported [1,13]. The overall cement DOH (in neat and blended cements) was calculated as $\mathrm{DOH} = \Sigma W_{\mathrm{i}} \Phi_{\mathrm{i}}$; where W_i is the weight fraction of the clinker phase i and Φ_i is the degree of hydration of the phase i at a given curing time.

3. Results and discussion

3.1. Overall degree of hydration of the neat portland cement from QXDA

The neat cements overall DOH is shown in Fig. 1. Increased temperatures accelerated the cement hydration in the early stages but in the later period an inversion of the DOH was observed in that the degree of hydration at higher

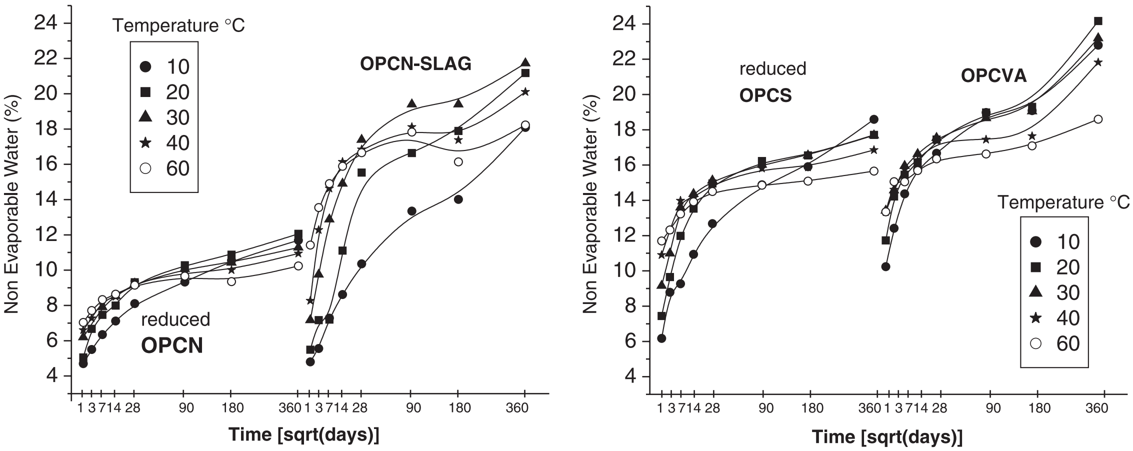

Fig. 2. Nonevaporable water vs. time for the slag and volcanic ash blended cements. Values of neat OPC were reduced according to the replacement level.

temperature attained lower degrees of hydration. This pattern has been previously reported and discussed for the hydration of alite and cement [1,16,20]. The two portland cements display different reactivities, but the basic characteristics of the hydration curves at different temperatures were very similar. The OPCS showed a slower start at 10, 20 and 30 °C, the gap in the DOH between the extreme temperatures at early stages was larger for OPCS. Generally OPCN appears to be more reactive in the first 14 days, and after this time the two cements surpassed the 50% of hydration at all temperatures.

3.2. Non evaporable water from TGA

The measurements of NEW for the neat portland cements displayed basically the same features as the DOH plots presented in Fig. 1. This was shown by the linear correspondence between DOH and NEW at all temperatures as represented in Fig. 3 to be further described.

Fig. 2 presents the NEW values for the neat cements and blends with VA and GGBFS, the curves of the neat cements were proportionally reduced according to the substitution level (e.g., OPCN values in Fig. 2 are 40% of the neat cement values). The NEW values for the slag blend were clearly higher than those of the corresponding neat cement fraction, probably due to the hydraulic reactions of the slag. For the OPCVA, the NEW values were higher than those of the neat cement fraction in the first 14 days of curing. It was previously reported [1] that the hydration of the cement fraction was accelerated, in decreasing order, in the presence of GGBFS, VA and PFA. Thus, the increased NEW values observed in the blended cements, are probably due to the combined effects of an enhanced cement hydration and to a contribution from the reactions of the replacement materials.

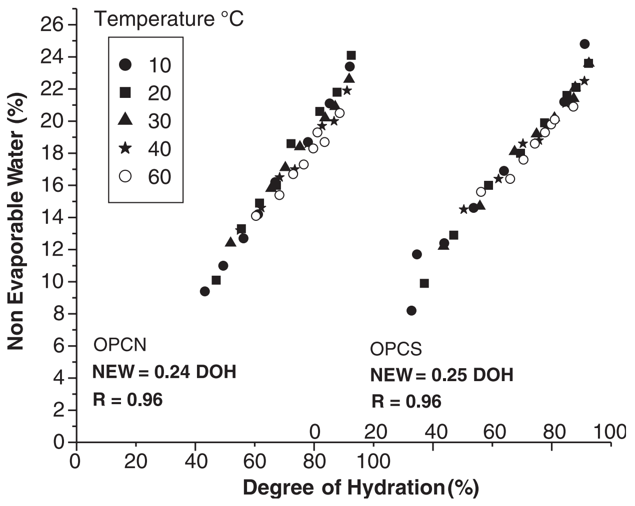

Fig. 3. Degree of hydration vs. nonevaporable water for both neat OPCs. Each data point represents a curing time.

Table 1
Data of overall degree of hydration and nonevaporable water for every temperature and each neat OPC

	10 °C		20 °C		30 °C		40 °C		60 °C	
	DOH	NEW	DOH	NEW	DOH	NEW	DOH	NEW	DOH	NEW
OPCN										
1	43.2	9.4	47	10.1	51.9	12.4	55.1	13.2	60.4	14.1
3	49.4	11.0	55.5	13.3	n.a.	n.a.	62.2	14.6	68.3	15.4
7	56.2	12.7	61.6	14.9	65.5	15.8	68.4	16.5	72.9	16.7
14	61.1	14.2	67.3	16.0	70.3	17.1	73.5	17.0	76.5	17.3
28	66.9	16.2	72.2	18.6	75.2	18.4	77.9	18.6	79.7	18.3
90	77.9	18.7	81.9	20.6	83.7	20.2	82.7	19.7	81.1	19.3
180	85.2	21.1	87.7	21.8	87.1	20.9	86.7	20.0	83.5	18.7
360	92	23.4	92.5	24.1	91.8	22.6	91.1	21.9	88.6	20.5
OPCS										
1	32.8	8.2	37.1	9.9	43.6	12.2	50.4	14.5	56.2	15.6
3	34.6	11.7	47	12.9	55.8	14.7	62.1	16.4	66	16.4
7	43.8	12.4	58.7	16.0	67.5	18.1	70.3	18.6	70.5	17.6
14	53.7	14.6	69.5	18.0	74.9	19.2	75.7	18.8	74.3	18.6
28	63.9	16.9	77.6	19.9	80.9	20.2	79.7	19.9	77.7	19.3
90	78.5	19.8	85.1	21.6	87.4	21.4	84.7	21.1	79.8	19.8
180	84.2	21.2	88.2	22.1	87.9	22.1	86.1	21.2	81	20.1
360	91.1	24.8	92.4	23.6	92.5	23.6	91	22.5	87.3	20.9
OPCN-30% PFA										
1	47.2	7.62	52.3	8.44	53.9	8.96	56.6	9.52	61.2	10.4
3	54.2	8.6	59	10.0	63.5	10.1	65.7	11.3	69.9	11.5
7	60.1	9.9	66.8	11.5	71.5	12.2	73.7	12.3	74.9	12.7
14	67.0	11.2	73.4	12.7	77	12.6	79.1	12.7	77.2	13.1
28	74.7	12.8	78.5	13.8	82	14.4	81.9	16.6	78.8	13.6
90	85.0	15.1	88.3	15.5	87.8	15.7	84.5	15.3	80.9	14.0
180	91.3	15.9	91.9	16.7	88.7	15.8	85.6	14.7	83.4	14.7
360	96.1	19.2	97.3	20.2	94.4	19.9	93.4	18.0	90.5	16.5
OPCN-60% GGBFS										
1	49.8	4.8	55.3	5.49	60.5	7.17	67.8	8.27	74.4	11.4
3	59.5	5.6	65.6	7.2	74.9	9.8	81.2	12.3	83.5	13.6
7	70.4	7.3	75.8	7.2	84.9	12.9	87.9	14.6	87.6	14.9
14	75.1	8.6	82.5	11.1	89.1	14.9	80.2	16.1	88.4	15.9
28	81.2	10.4	88.3	15.5	92.3	17.4	92.7	16.9	88.3	16.7
90	89.0	13.4	91.5	16.6	95.1	19.4	93.6	18.1	90.4	17.8
180	89.6	14.0	91.3	17.9	94.1	19.4	92.7	17.4	90.6	16.1
360	93.2	18.1	97.3	21.2	97	21.7	96.4	20.1	92.9	18.2
OPCVA										
1	50.3	10.24	55.3	11.73	61.5	13.42	63.5	13.33	66.1	13.4
3	59.7	12.4	64.8	14.2	69.5	14.6	71.1	14.6	73.6	15.1
7	68.4	14.4	72.8	15.5	77.2	16.0	77.9	15.8	77.3	15.1
14	74.1	15.8	78.1	16.2	82.5	16.6	82.6	16.3	80.1	15.7
28	79.4	16.7	83.4	17.5	87.1	17.5	85	17.4	81.7	16.4
90	89.6	19.0	92.1	19.0	91.3	18.7	87.8	17.5	84.1	16.6
180	94.4	19.1	94.4	19.3	92.8	19.1	89.4	17.6	86.2	17.1
360	98.8	22.8	98.2	24.2	97.6	23.2	95.8	21.8	93	18.6

Both in percentage values.
n.a. = not available.

3.3. Estimation of the nonevaporable water of the cement replacement materials

Fig. 3 plots data of DOH vs. NEW for both neat cements, for every temperature and curing age. For each OPC, the data of the five hydration temperatures adhered to a linear fitting, this suggests that for a given cement DOH, the paste retains very similar amounts of water regardless of the hydration temperature. The slopes of such linear regressions were near the value of 0.23, which is the nonevaporable water proposed in the model of Powers [21] for a fully hydrated paste. The good linear correspondence for DOH–NEW allows to obtain the equations indicated in Fig. 3 to predict either value as a function of the other.

Kjellsen et al. [22] observed that the ratio chemically bound water to the DOH was not significantly influenced at 70% hydration at 5, 20 and 50 °C. The results from Fig. 3 can be correlated with previous observations (by scanning electron microscopy in backscattered mode) where it was noted [1] that the C-S-H rims of hydration products formed at 10 °C where darker than those formed at 60 °C. As it seems that amount of NEW is essentially independent of the hydration temperature for a given degree of hydration, then the products formed at 60 °C could actually be more compact than at 10 °C, and perhaps truly blocking further hydration of the cement grains at the higher temperature as pointed by Escalante-Garcia and Sharp [1].

In blended cements, for each time of hydration corresponds a set of a DOH (cement fraction) and a NEW_T (total) value. The latter can be considered as composed of two parts: $NEW_T = NEW_C + NEW_R$, where NEW_C is the contribution from the portland cement fraction, NEW_R is the contribution from the replacement material. Assuming that the cement hydrates retain similar amounts of water whether as neat or blended, for each blended cement, the contribution NEW_C could be predicted by extrapolating the models NEW–DOH (from Fig. 3) for the DOH of the cement fraction in the blended cements. Then, NEW_R can be calculated by the simple algebraic operation $NEW_T - NEW_C$. Table 1 presents the tabulated data of DOH vs. NEW for the neat and blended cements, as used in the estimations of NEW_R.

Fig. 4 presents the results of the estimated NEW_R, from the replacement material fraction for the three blended cements. The slag data indicates that it takes substantial amounts of water and that its hydration rate is temperature dependent. In early ages the slag NEW_R were higher as the temperature increased; however, in the later ages the for the slag cured at 60 °C lower NEW_R values were noted compared to the other temperatures, except 10 °C. This pattern was similar to that observed in the DOH of the neat cements (Fig. 1) and suggests that some mechanism slowed down the hydration of the slag grains at 60 °C. Rims of hydration products were observed around slag grains at 30 and 60 °C in this cement [23]; the latter showed a brighter gray level in backscattered electron images; it was considered that the hydration products formed at 60 °C were more compact (than at 30 °C). Such hydration products could be operating as barriers for further slag hydration. The curves for slag NEW_R (Fig. 4) also showed a very similar pattern to those of compressive strength development observed for the slag cement [23], this brings about the importance of the slag hydration reactions in the strength development of the blended pastes.

Contrasting with the slag results, the estimated NEW_R values for both pozzolanic materials were relatively low with values below 2.5% for up to 180 days; after 360 days the data plotted at about 4–5%. This suggests that the hydration products produced from the pozzolanic reaction had small water intake other than that from the CH. The predicted NEW_R obtained for the pozzolanic materials, indicates that the enhanced NEW_T observed, in the blended cements with respect to the neat cements, was due mostly to enhanced hydration of the cement fraction as reported previously, where evidence of pozzolanic behavior (CH consumption) was also provided [1].

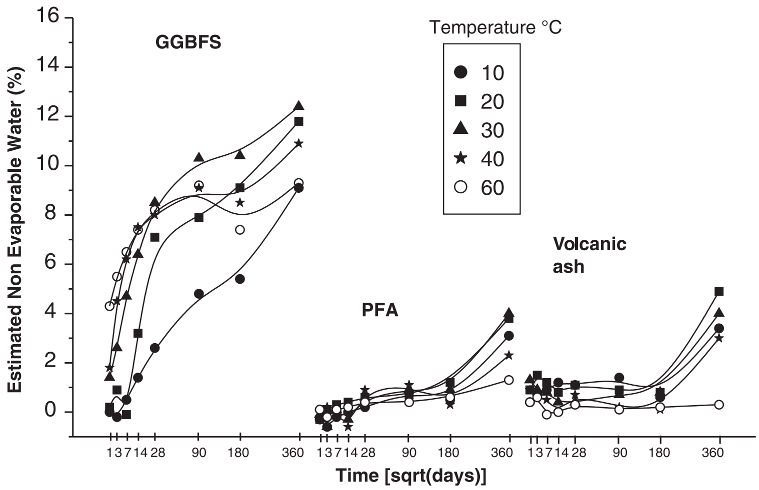

Fig. 4. Estimated nonevaporable water values vs. time for the replacement materials.

A report that used PFAs with CaO contents 9–24% [24] concluded that for some fly ashes the pozzolanic reaction in hardened cement paste changed the chemically bound water content: the water provided by the CH is not the only water that takes part in the reaction. Uchikawa [25] quoted that for a fly ash cement containing a high-calcium PFA, the reaction rate, estimated from the amount of combined water, was higher than that of a fly ash containing an ordinary PFA. In this case the pozzolanas had less than 2%CaO. It seems that the amount of water fixed by the reaction of a pozzolana is related to the high CaO content. High CaO PFA may contain free lime, anhydrite, C_3A, $C_4A_3\bar{S}$ and calcium silicates [26] and show intrinsic cementitious behavior, such phases taking water to form hydration products. Thus, the interpretation of NEW in blended cements must be cautious and with consideration of the chemical composition of the replacement material or mineral admixture.

4. Conclusions

1. For the two 2 neat cements, nonevaporable water and overall degree of hydration showed a linear correlation at temperatures 10–60 °C, confirming that the former can be used as a relative but real indicator of the degree of hydration of a cement paste. Such linear fitting indicated that, for a given degree of hydration, the pastes retained very similar amounts of nonevaporable water, regardless of the hydration temperature.
2. The equations of such linear fitting of experimental data allowed to estimate the amount of nonevaporable water of the cement fraction in blended cements; then by difference from the total nonevaporable water, the contribution from the replacement material could be estimated. The estimated results showed:
    - (a) The hydraulic nature of the GGBFS, the patterns of estimated nonevaporable water were similar to those of the neat cement. In the first days, higher NEW values were noted at higher the temperatures; however, this was inverted in the long term. This suggested that a mechanism slows down the slag hydration at 60 °C in the long term, while at 10 °C such process appears to be progressing after 1 year.
    - (b) The estimated nonevaporable water from the pozzolanic materials suggested that small amounts of additional water were needed in the pozzolanic reaction to form additional C-S-H.
3. In virtue of the differences in nonevaporable water with results from other reports, that worked with high CaO PFA's, it is apparent that the CaO content in the pozzolanas plays an important role in the binding of additional water; possibly due to the presence of cementitious Ca-bearing phases that hydrate directly taking in additional water.

Acknowledgements

Thanks are due to CONACyT México and the British Cement Association for their financial support.

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