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

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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

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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–

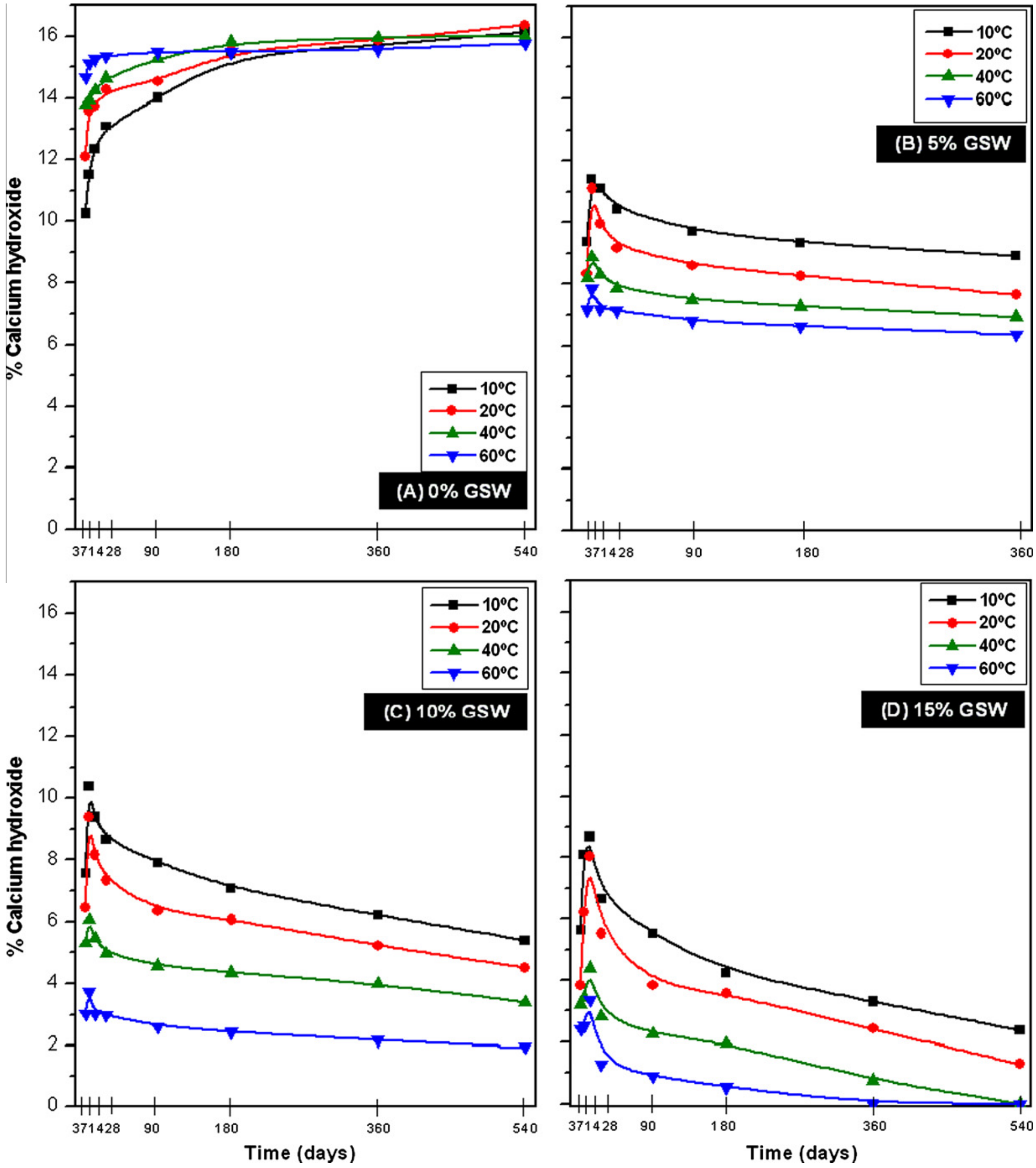

Fig. 1. Calcium hydroxide content vs. time of the neat and blended cements (normalized) cured at 10, 20, 40 and 60 °C.

14 days, reaching maxima and then were depleted (see Fig. 1). This provided evidence of the pozzolanic behavior of the silica waste since the first days of hydration. Moreover, the normalized CH contents in the blended cements were lower than the neat cement since 3 days of hydration.

The CH consumption was greater as the GSW load increased, and for 15% GSW all of the CH was consumed after 180–540 days, indicating a strong pozzolanic behavior. Similar results of CH depletion were reported for a SF with replacement level of 30% [3].

3.1.2. Effect of temperature

The results show that the pozzolanic reaction was strongly affected by the curing temperature. As indicated above, for all blended cements the CH contents increased for the first 7–14 days and dropped afterwards. The maximum CH concentration values reached were lower as the curing temperature increased, and in general the lines of CH vs. time plotted lower as the temperature increased; this indicates that the reaction was accelerated by the temperature. The observed trend towards lower CH concentrations for the 10 and 20 °C and for all GSW loads suggests that the pozzolanic reaction was still in progress even after 540 days of hydration.

The behavior of CH contents described with respect to the effect of temperature and the replacement level were similar to those previously reported for in cement pastes with SF [3,5] and other replacement materials [15].

3.2. Nonevaporable water

Fig. 2 presents the results of the NEW content vs. time for all blended and the neat cements. The results for the neat cement

(Fig. 2A) were similar to those reported by other authors [11]. The highest NEW value was of 23.8%, which already considers a correction factor due to the decomposition of the admixed $CaCO_3$ previously mentioned. The theoretical NEW value reported for neat cement is approximately 23% for a w/s ratio of 0.50 [16]. For the neat cement, the NEW augmented markedly with the increasing temperature at short hydration periods (i.e. after 3 days, the NEW at 60 °C was 17.3% higher than at 10 °C); however, the inverse was observed at longer hydration periods (i.e. after 540 days, the NEW at 10 °C was 5.3% higher than at 60 °C). This indicates that at higher temperatures there is an initial higher rate of formation of hydration products (HP) in the early stages; but later the hydration is slowed down with the formation of dense layers of HP around the cement grains. In contrast at the lower temperatures, the HP formation continues resulting in higher NEW values at longer hydration periods. Also, the NEW values could indicate higher amounts of HP or higher amounts of water bound in similar amounts of HP.

The results for NEW can be used to estimate the degree of hydration (DOH) for the neat portland cement. This is achieved by referring the NEW to 24% (the maximum value obtained in the results assuming complete hydration); the results are shown in Fig. 3. From the results it can be noted that the temperature has an important effect: at 3 days the DOH were higher for 40 and 60 °C (≈72% for 60 °C vs. 62% for 20 °C), but at 180 days the results were very similar and for the later hydration periods the DOH was higher at lower curing temperatures.

For blended cements the NEW contents would also include the contribution of the replacement materials, and thus in this case

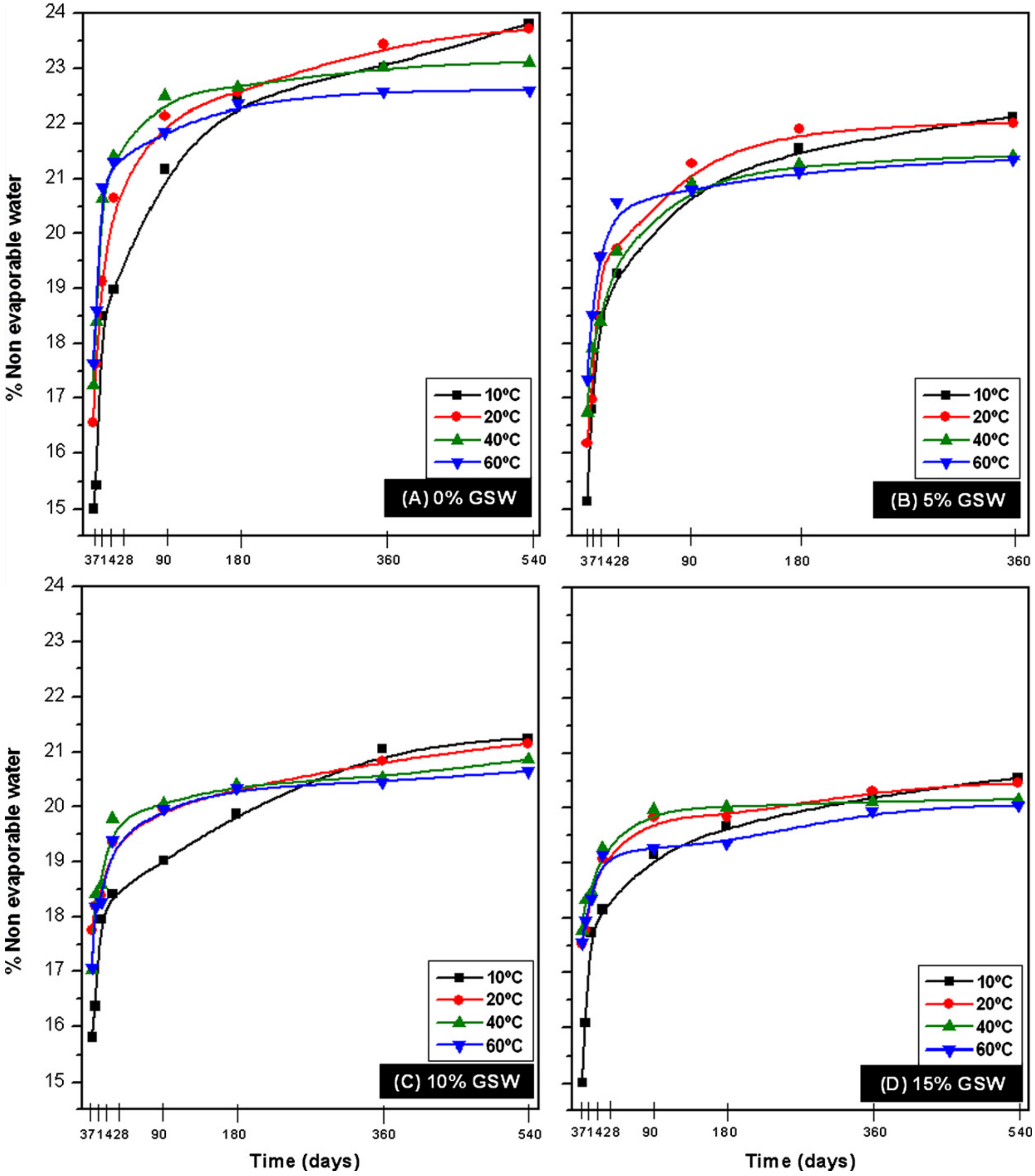

Fig. 2. Nonevaporable water content vs. time for the neat and blended cements. Data is reported relative to the ignited weight.

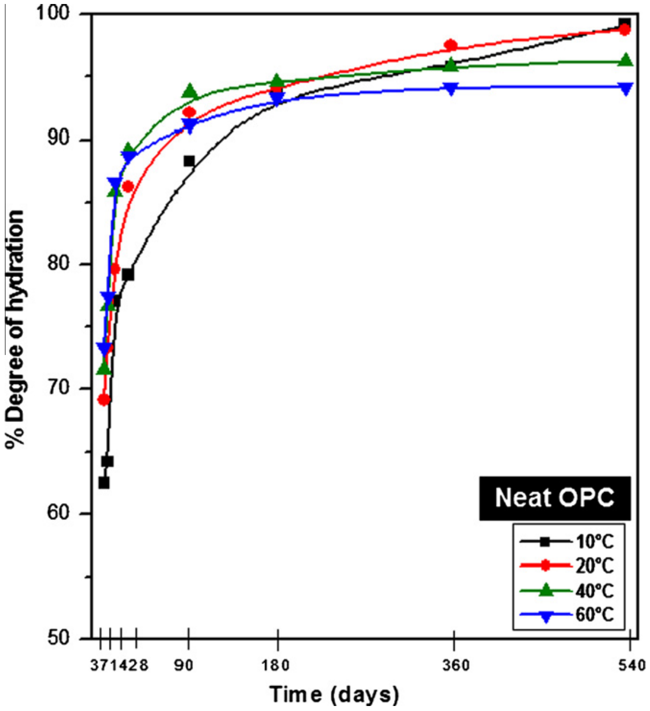

Fig. 3. Estimated degree of hydration vs. time for the neat cement.

NEW only gives a semi-quantitative indicator of the hydration of the composite cements. Moreover, the comparison of NEW between pozzolanic blended cements and the parent cement is not totally correct due to the differences in the composition and the degree of polymerization of the C–S–H gel, and also to the CH depletion due to the pozzolanic reaction. The results of NEW for the blended cements are presented in Fig. 2B–D. One initial observation is that these results were lower than those of the neat cement, especially at higher silica loads and longer hydration periods; the results are described as follows:

3.2.1. Effect of temperature

The effect of the temperature in all blended cements was the same as described for the neat OPC; i.e. increased values in early hydration periods at higher temperatures, but at longer periods of hydration, a temperature inversion occurred and the NEW values were higher for the lower temperatures. The explanation of this could be attributed to similar mechanisms as those described for the OPC. For the paste with 5% GSW, at 3 days the NEW contents at 60 °C were 15% higher compared to the 10 °C values; however, at 360 days the latter were 4% higher than the former.

3.2.2. Effect of replacement level

The NEW contents were lower with increased GSW load. As explained before, this behavior was attributed to several factors, as the modified polymerization of the C–S–H and the depletion in the CH content. The latter is further considered in the next section by means of a comparison of results of NEW with and without the CH contributions. Also, for the first 7 days the NEW was slightly higher for 10% and 15% of GSW, but after 14 days, this was reverted and the NEW values of 0% and 5% GSW were higher. This initial increase in the NEW could be associated with an acceleration of the cement hydration, which is possible as the nanometric particles of the GSW could act as nucleation sites and also provide new C–S–H gel from its pozzolanic reaction.

3.3. NEW values vs. CH consumption

As mentioned before, the NEW results of the blended cements were lower compared to the neat cement. This apparent decrease in the reactivity of the cements blended with SiO_2 rich materials could be attributed to several factors including those described in the introduction [2,4,5,8,11]. Moreover, Lu et al. [7] proposed that SF participates in three reactions: (a) with the C_3S and water to form one type of C–S–H; (b) with the CH to form a different C–S–H; and (c) with the existing C–S–H to yield a further modified hydrate. After this, the SF system combines less water per gram of cement. Therefore, the SF serves to lower the amount of bound water in the system.

From the above, a combination of the proposals of references [5,7,8] were considered appropriate to explain the results, since the reduction of CH contents (Fig. 1) took place with reduction of the NEW values, and a direct comparison of NEW among neat and blended cements is not possible. It is also possible that C–S–H hydrates with different water contents are formed as described in [7]; and the C–S–H from neat cement possibly contains higher amounts of water than C–S–H involving the participation of the pozzolana.

A more suitable direct comparison would be that in which the NEW values excluded CH water losses, this would allow comparing the NEW derived only form the hydrates from both blended and neat cements. On this basis, the values of the NEW results were modified by subtracting the CH water losses. Fig. 4 presents modified NEW values (mNEW) vs. time for the four replacement levels and all temperatures. The following observations are noteworthy:

3.3.1. Effect of replacement level

During the first 28 days of curing, the mNEW were greater in the presence of the GSW, compared with the neat cement. This suggests that the presence of the GSW accelerated the cement hydration, acting as nucleation sites [17] for deposition of the HP; additionally the GSW formed new HP by consuming CH, which could be retaining water and favoring the further hydration of the calcium silicates. After 180 days the results were similar for all the GSW loads.

3.3.2. Effect of temperature

Comparing Figs. 3 and 4 a similar behavior with regards to the temperature is observed for the neat cement and that with 5% GSW. For the former, the NEW and mNEW increase with the temperature for the first 90 days and presented an inversion for latter hydration periods, obtaining higher values of mNEW at curing temperatures of 10 and 20 °C. For the latter, a similar pattern was noted, with a temperature inversion after 90 days, but obtaining similar values of mNEW at 360 days for all curing temperatures.

For the cements with 10% and 15% GSW the temperature effect was more noticeable for the first 28 days of hydration. Nevertheless, the temperature inversion was not observed in these cements, giving higher mNEW contents for the higher temperature for up to 360 days, and similar mNEW contents at 540 days. This behavior indicates that the cement hydration and the pozzolanic reaction are favored by increasing temperatures in blended cements with high silica loads.

3.3.3. Comparison between NEW and mNEW

In order to compare the values from the plain NEW measurements and those of the NEW from the hydrates, Fig. 5 presents the plots of NEW vs. mNEW for all curing temperatures; data from the neat cement is also included for comparison purposes. As described in the above section, several authors suggested that the pozzolanic reaction does not bind additional water while some other pointed the opposite. Therefore, this comparison

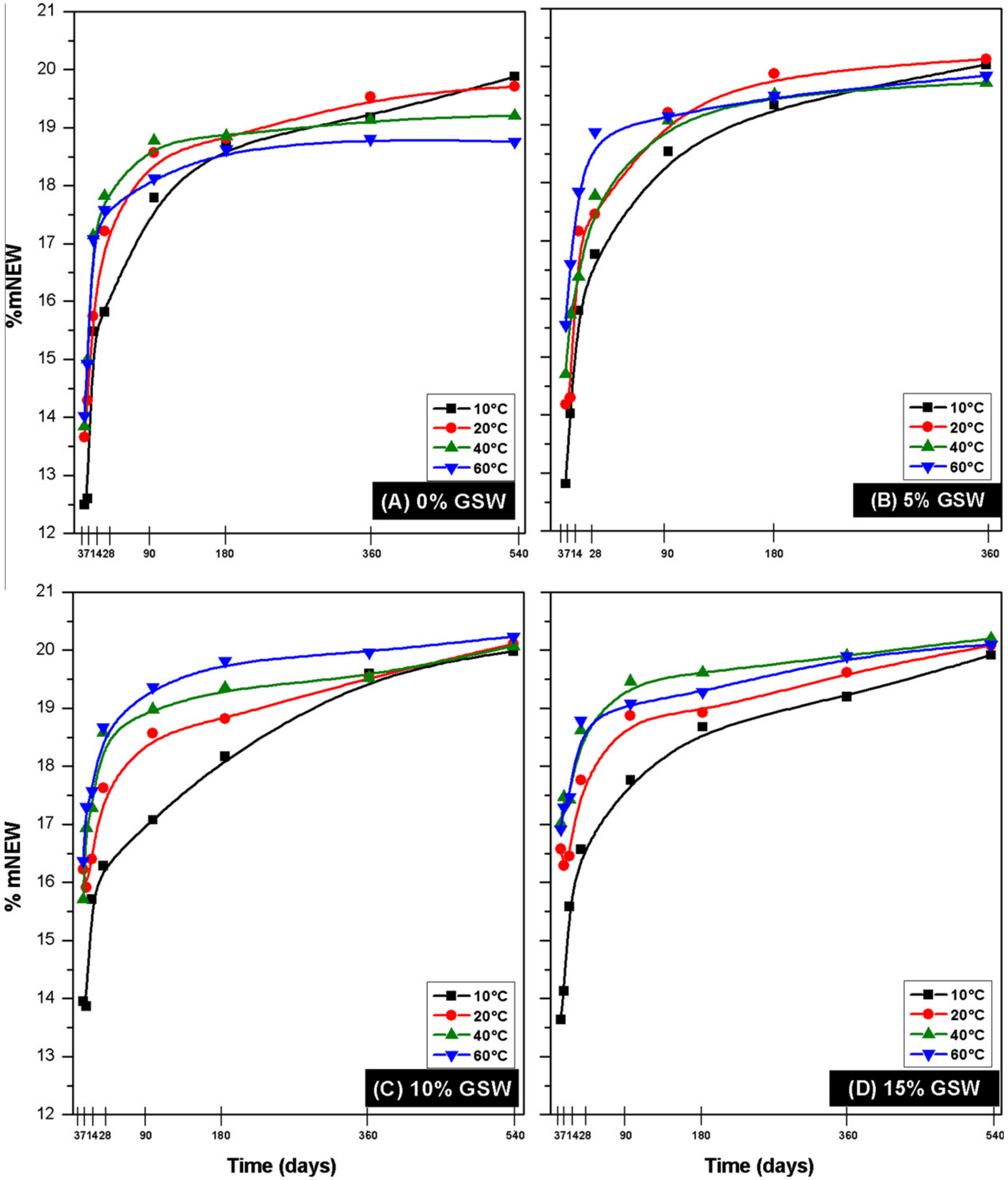

Fig. 4. Nonevaporable water content from the hydrates vs. time for the neat and blended cements. Data is reported relative to the ignited weight.

could help providing a better understanding of whether or not the pozzolanic reaction is consuming water in the systems GSW–OPC.

Fig. 5 shows that for a fixed NEW content, the corresponding mNEW values were higher for the blended cements, and were also higher for increased GSW contents and higher temperatures (which corresponds to the CH depletion trends plotted in Fig. 1). Any excess of mNEW over NEW is due to a mixed effect of the additional C–S–H formation (by CH consumption) and also by accelerated OPC hydration reactions; however the contribution of the pozzolanic reaction cannot be quantified.

Also in Fig. 5 it can be observed that in order to obtain similar values of mNEW for the neat and blended cements at 360 days of hydration (~20%, see doted line), the differences of the NEW values varies ~8% for the neat and blended cement with 5%GSW to ~15% for the neat and blended cement with 15%GSW, with a slight difference with the temperature.

The comparison among mNEW and NEW indicate that the consumption of CH has a strong influence in the values of NEW obtained from cements blended with pozzolanic materials. It seems that in order to analyze the effect GSW in the cement hydration is better to use the data of mNEW, and the effect of the NEW reduc-

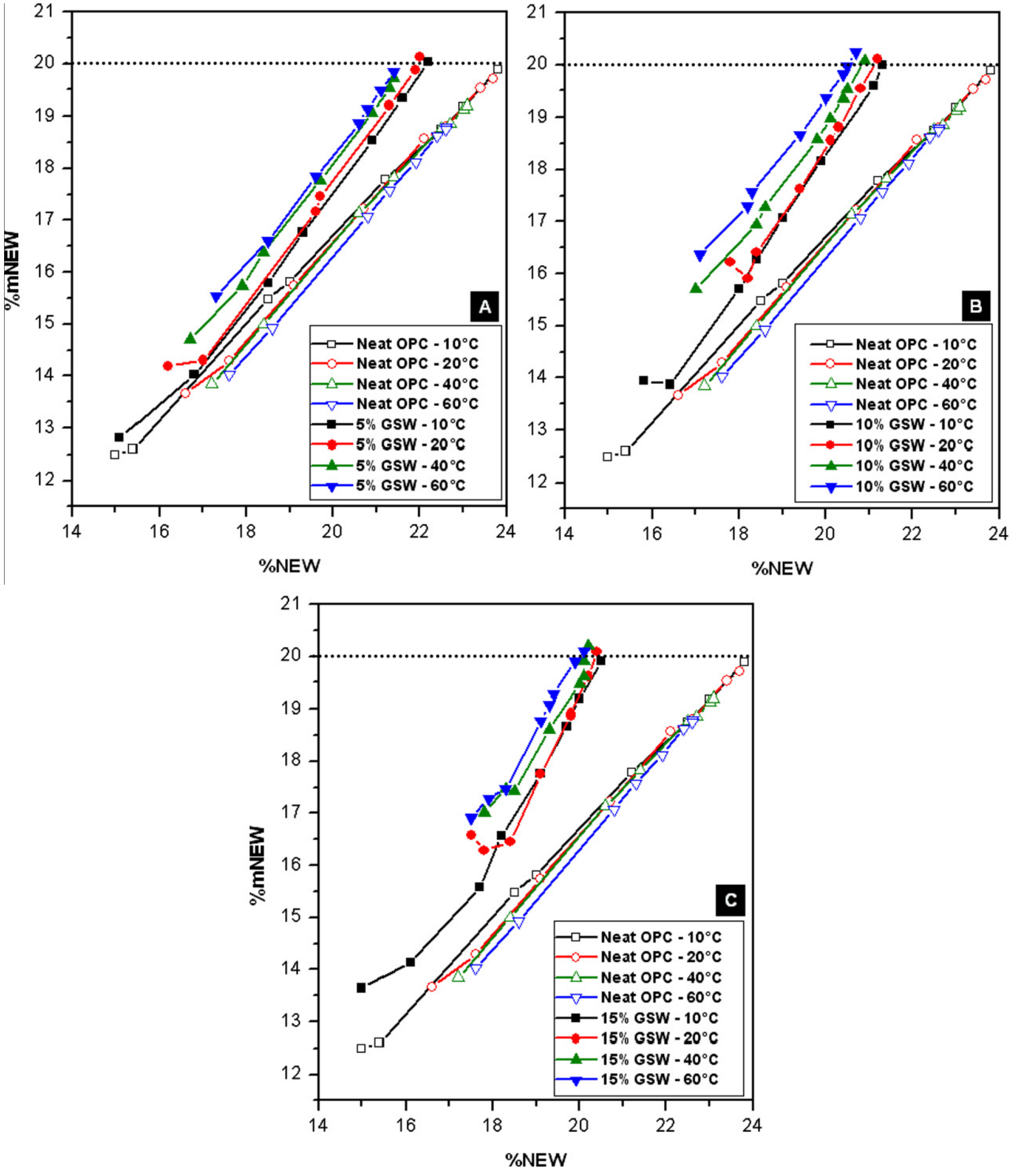

Fig. 5. NEW vs. mNEW for the neat and blended cements.

tion could be associated to the pozzolanic behavior of the silica by the reduction of the CH.

4. Conclusions

The reactivity of a geothermal silica waste as a replacement of portland cement was evaluated, under different curing temperatures, evaluating the nonevaporable water and calcium hydroxide contents. The results of the investigation provide the following conclusions:

- The nonevaporable water (NEW) from the neat cement increased with the curing temperature in the early ages; however it showed an inversion after 180 days. The highest value of 23.8% at 540 days was obtained at 20 °C. A similar pattern was noted for the cement pastes with GSW.
- The calcium hydroxide (CH) formation was also accelerated by increases in temperature and with a slight temperature inversion after 360 days, similar CH contents were attained at all temperatures up to 540 days.

- The geothermal silica waste presented pozzolanic activity, consuming CH; this was strongly influenced by the curing temperature and the replacement level. The pozzolanic reaction was highly accelerated by increases in temperature.
- The nonevaporable water results (NEW) for the blended cements were lower compared to the neat cement.
- Modified NEW (mNEW) values, excluding CH water losses, were higher than the plain NEW measurements. The comparison between mNEW vs. NEW results suggested that: (1) the pozzolanic reaction products incorporate water due to additional C–S–H formation by CH consumption and (2) the cement hydration was accelerated by the presence of GSW particles and CH consumption.

Acknowledgement

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