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Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions

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Abstract

Pastes of blended cements, with 30% and 50% slag and water:solids ratios (w/s) of 0.50 and 0.35, were hydrated at 10°C, 30°C and 50°C for up to 6 months. The reactivity of the slag fraction increased with the hydration temperature, w/s ratio and with a reduction of the replacement level of the slag. The more reactive of two slags used was that having the highest vitreous fraction; its highest degree of reaction observed was 50%, at 50°C, 30% slag and w/s ratio of 0.50, while the lowest degree of hydration was approximately 20% at 10°C, 50% slag and w/s ratio of 0.35.

Keywords: Slag reaction; Chemical dissolution; Blended cement; Hydration temperature; Granulated blast-furnace slag

1. Introduction

Blast furnace slag has been widely used as a successful replacement material for Portland cement, improving some properties and bringing environmental and economic benefits. The production of the pig iron production has increased progressively in the recent years. Considering that approximately 300 kg of slag are generated per ton of iron [1], it is estimated that about 1.4 million are produced yearly by the two largest steel companies.

There have been many studies concerning the hydration and microstructure of Portland cement–slag systems [2–5]. A better understanding of their hydration requires knowledge of how the slag reacts.

The reacted fraction of the slag in blends with Portland cement hydrated under various hydration conditions have been reported by several researchers. As several hydration parameters and slag characteristics may affect slag reactivity, it is common to keep some parameters constant while varying others. Luke and Glasser [6] studied pastes with 30% of slag at temperatures 25–55°C hydrated from 0.5 to 24 months; the percentage of reacted slag initially increased with temperature. They also pointed the probability of a rapid reaction within the first week and observed that 40–50% of the slag had reacted after 1 month. Battagin [7] hydrated a blend with 50% slag in a range of temperatures of 23–80°C for up to 28 days. He observed that the slag hydration increased systematically with temperature; after 21 days, about 35% and 60% of the slag had reacted at 23°C and 80°C, respectively. Hinrichs and Odler [8] employed DTA and used several slag loads and slag finenesses. They indicated that, given the accuracy of the method, no significant differences were noted on the hydration of the slag at different slag/clinker ratios, which was similar to the results by Battagin [7]. At increased fineness of slag, its reactivity also increased. Lumley et al. [9] reported an extensive study varying some characteristics of the slag, the slag load, water:solids ratio (w/s) and employed various Portland cements. They observed that at w/s of 0.40–0.60 and 20°C, 30–50% of the slag had reacted after 28 days; similarly, 45–75% had reacted in 1–2 years of hydration. Taylor [10] presented a summary from the literature of results of reacted slag highlighting differences in results between several workers.

One of the main methods for the estimation of the degree of reaction of the slag are those based on a preferential chemical dissolution of the reaction products and unhydrated cement. By means of a comparative study, Luke and

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Glasser [11] assessed various methods available for the estimation of the reacted fraction of slag, they concluded that the EDTA based modified method of Demoulian was the most suitable. More recently, Lumley et al. [9] reported a study in which they employed a further modification of the method of Demoulian.

Most of the results found in the literature cover groups of parameters for hydration conditions, for example, temperature of hydration, w/s, percentage of slag replacement and slag characteristics such as its vitreous fraction, chemical composition and fineness. Aiming to complement the information available on the reactivity of the slag, this paper presents results that included a combination of hydration temperature, w/s, slag vitreous fraction and slag replacement level for blended cement pastes hydrated for up to 6 months. The method used for the determination of the degree of hydration of the slag was essentially that reported by Luke and Glasser [11] in order to obtain comparable results.

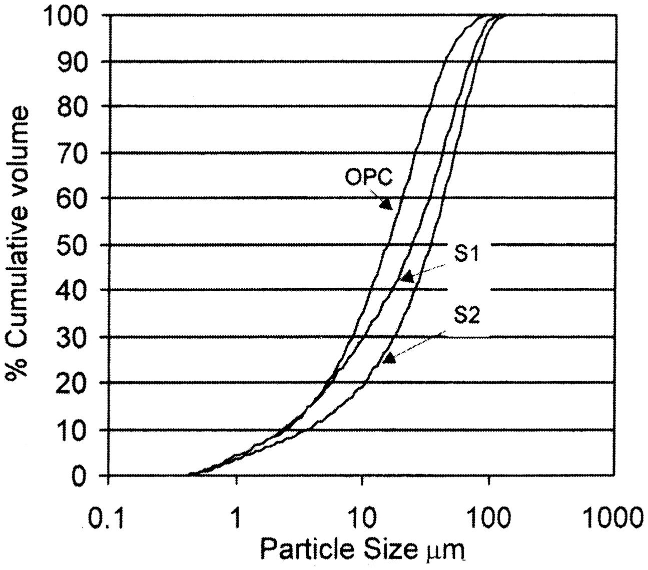

Fig. 1. Particle size distribution of the starting materials.

2. Experimental procedure

2.1. Materials

One ordinary Portland cement, provided by Cementos Apasco Ramos Arizpe, and two blast furnace slags, supplied by Altos Hornos de México (AHMSA) Monclova, were employed. Both slags were obtained directly from the steel works, from two separate runs of the blast furnace and hence were labeled S1 and S2. The oxide composition of the slags and cement is presented in Table 1. In order to obtain different vitreous fractions in the slags, these were sampled and maintained in the spoon exposed to ambient temperature for 30 s and 6 min for S1 and S2, respectively. The slags were subsequently quenched in water. Phase compositions as obtained from QXDA are also reported in Table 1. The resulting vitreous fraction was estimated as the difference from the total of the crystalline fraction. S1 had 97% vitreous fraction while S2 had 53.5%. Prior to the preparation of the blends with cement, the slags were ground in the laboratory in a rotating ball mill, the same conditions were applied to both slags. The resulting particle size distribution, as obtained from Laser Diffraction (Coulter LSQ100), is presented in Fig. 1. The slags size distributions were fairly similar, but slightly coarser than that of the cement.

2.2. Hydration

The dry powders of Portland cement and slag were blended in the laboratory, Table 2 gives full details of the combination of slag-cement and w/s used. Additionally, the neat cement was also hydrated as a reference. The initial hydration was performed at ambient temperature 23 ± 2°C. After the addition of the water, the pastes were kept in

Table 1
Oxide and phase content of the starting materials

	Oxide composition				Phase composition		
	OPC	S1	S2		OPC	S1	S2
SiO_2	19.8	35.3	32.5	Alite	70.5		
Al_2O_3	5.8	11.4	10.7	Belite	12.0		
CaO	65.1	33.9	37.3	C3A	3.5		
MgO	2.1	13.8	14.1	C4AF	10.5		
Fe_2O_3	2.3	1.7	1.9	Gypsum	2.5		
MnO	0.1	1	0.6	Monticelite		0.5	4.0
TiO_2	0.2	1.2	0.9	Quartz		0.5	0.5
K_2O	0.7	0.9	0.3	Mullite		0.5	29.0
Na_2O	0.6			Melilite		0.5	2.0
SO_3	2.6			Merwinite			11.0
	99.3						
Total	99.3	99.8	98.7	Total	99.0	3.0	46.5
Hydraulic Index		1.84	1.94	Glassy fraction		97.0	53.5

Table 2
Combinations of cement and slag and hydration conditions for the blended cements

	a/s = 0.35						a/s = 0.5					
	30% slag			50% slag			30% slag			50% slag		
Slag	10°C	30°C	50°C	10°C	30°C	50°C	10°C	30°C	50°C	10°C	30°C	50°C
S1	x	x	X	x	x	x	x	x	x	x	x	x
S2							x	x	x	x	x	x

motion in plastic bags for 7 h to avoid the segregation of water. After setting, cubes of approximately 1.5 cm were cut, randomly grouped and then transferred to plastic containers with distilled water, which were submerged in isothermal water baths at 10°C, 30°C and 50°C. This was considered as the starting time for curing.

2.3. Characterization

After curing periods of 3, 7, 14, 28, 90 and 180 days, three cubes were randomly sampled from the plastic containers at each temperature of hydration. Approximately 60 g were hand ground to a relatively fine powder and placed in a small plastic bottle, 25 ml of acetone were added to arrest the hydration. The specimens were further dried at 105°C for 5 h in a stove. Once dried, the specimens were further ground to pass a 106-μm mesh, with cycles of grinding-sieving and regrinding the unpassed material. The powders were mechanically homogenized after grinding and the characterization was performed on the samples after this stage.

2.3.1. Selective dissolution

The reactivity of the slag was estimated by dissolving hydration products and unhydrated cement, the procedure employed was essentially that based on EDTA as described by Luke and Glasser [11]. Agitation of the solutions was promoted with a propeller, which resulted in reduced dissolution times without affecting the reproducibility of the results. Samples of 0.25 g were subjected to the dissolution process, a precision of 0.0001 g was used in all weighing operations. The results were referred to the ignited weight of the sample. The percentage of reacted slag was calculated with the following formula:

$$\%\text{Reacted Slag} = 100 - \frac{W_{\text{ur}} + \frac{(P_{\text{rs}})(\%\text{Slag})}{100}(W_{\text{s}}) - \frac{(P_{\text{rc}})(\%\text{cement})}{100}(W_{\text{s}})}{(W_{\text{s}})(\%\text{Slag})}100$$

Where: W_{ur} = weight of undissolved residue of the blended cement at every age, W_{s} = weight of the sample (ignited weight), P_{rs}=% dissolved unreacted slag, P_{rc}=% undissolved cement residue, %slag = percentage of slag in the blended cement, %cement = percentage of cement in the blended cement.

It was considered that the crystalline fraction of the slag remains unreactive. P_{rc} was determined separately at each time of hydration, the results ranged from 6% to 8%. P_{rs} was 5% and 11% for S1 and S2, respectively. No corrections were attempted for hydrated phases present in the undissolved residue, which may lead to an overestimation of the unreacted fraction. Repetition runs of the dissolution procedure were performed on unhydrated cements with 0%, 10%, 20%, 50%, 80% and 100% slag loads to check the reproducibility of the technique. The results indicated standard deviations lower than 10% with respect to the average value.

2.3.2. Nonevaporable water (NEW) and calcium hydroxide

NEW was estimated from the loss on ignition at 950°C. Samples of 1 g were weighed with 0.0001 precision, dried at 130°C for 1 h and then ignited at 950°C for 20 min. The NEW was estimated as 100(weight$_{130^\circ\text{C}}$ − weight$_{950^\circ\text{C}}$)/weight$_{950^\circ\text{C}}$. CH was estimated by means of thermal analysis using a thermobalance (Model TG7, Perkin Elmer). Samples of 35 mg were heated at 15°C/min to 900°C. The mount of CH was estimated from the step of weight loss occurring at 450–550°C [12].

3. Results and discussion

3.1. Percentage of reacted slag

Repetitions were performed on 29 of the 96 hydrated samples that were generated during the experimentation, the deviation from the average of three experiments was always lower than 5%. The results of percentage of reacted slag as a function of time for the blended cement with S1 are presented in Fig. 2, for all the temperatures and w/s. There was general pattern in that at higher hydration temperatures, the reactivity of the slag was increased, as can be seen in the sets of curves A, B, C and D. The increased slag reactivity with higher temperatures is a commonly reported feature of blast furnace slag [6,7,13]. With regards to the water available for the reactions, it can be noted in Fig. 2 that the slag reactivity was also increased at higher w/s, compare curves A–B and B–D. This effect was similarly reported by Lumley et al. [9]. This may be similarly due to the fact that as the w/s is increased the cement reactivity is also increased [14], as there is more space available for hydration product to form [15]. As the cement hydration is increased, this may bring an enhancement of the cement-activating environment for the reaction of the slag.

It can also be noted that in Fig. 2 for a fixed w/s the percentage of reacted slag was lower for the higher replacement level of 50%, compare curves A–B and C–D. Such

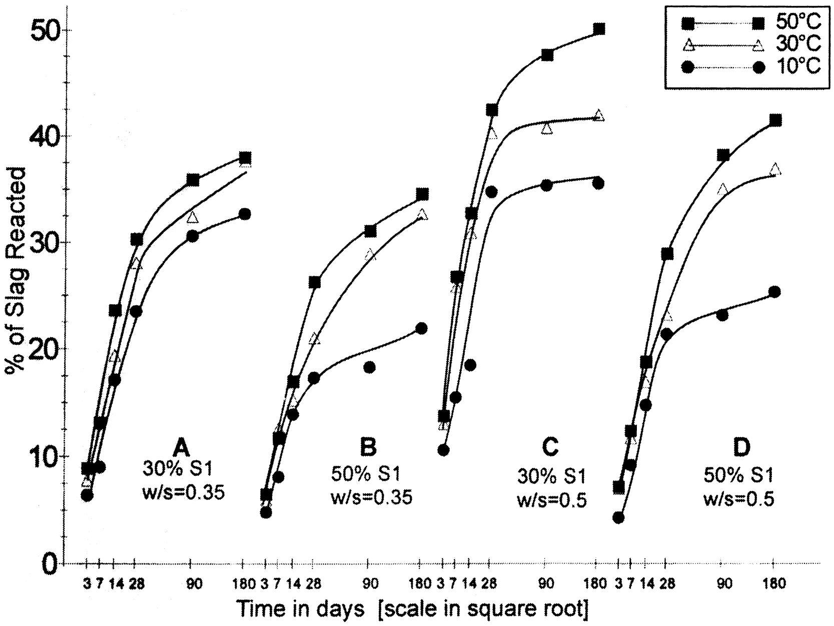

Fig. 2. Percentage of reacted slag versus time for blends of cement with slag S1.

effect was more marked at w/s = 0.50. In addition to the presence of more water, as mentioned before, it can also be considered that the alkaline activating effect of the cement would be greater at lower slag loads, i.e., 30%, than for the cement with a higher slag load.

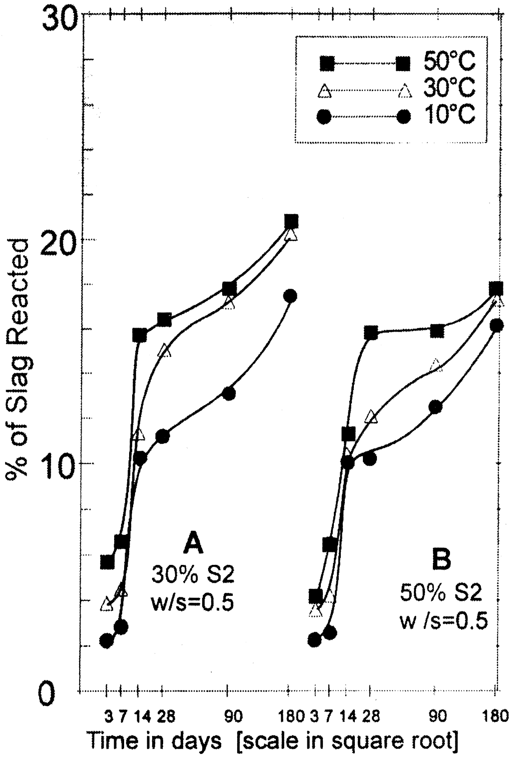

Fig. 3. Percentage of reacted slag versus time for blends of cement with slag S2.

Hinrichs and Odler [8] reported that the percentage of slag did not have a significant effect on the slag reactivity in the range of 30–60% but the reactivity reduced at 80% slag. The results from Battagin [7] indicated that the blend with the lowest slag replacement had the lowest slag reactivity between 14 and 180 days. The percentage of reacted slag as a function of time for the cement blended with S2 is presented in Fig. 3. For this cement, only one w/s = 0.50 was employed, the effects of the temperature and the effect of slag load on the reactivity of the slag were similar as those described for the cement with S1.

Analyzing the effect of the slag vitreous fraction on its reactivity, by comparing the curves C and D from Fig. 2 to the curves A and B in Fig. 3, respectively, it can be seen that

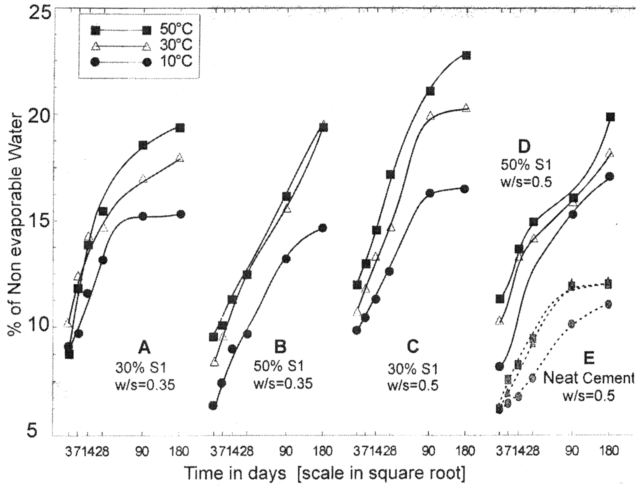

Fig. 4. NEW versus time for blends of cement with slag S1 values for the neat cement in dotted lines.

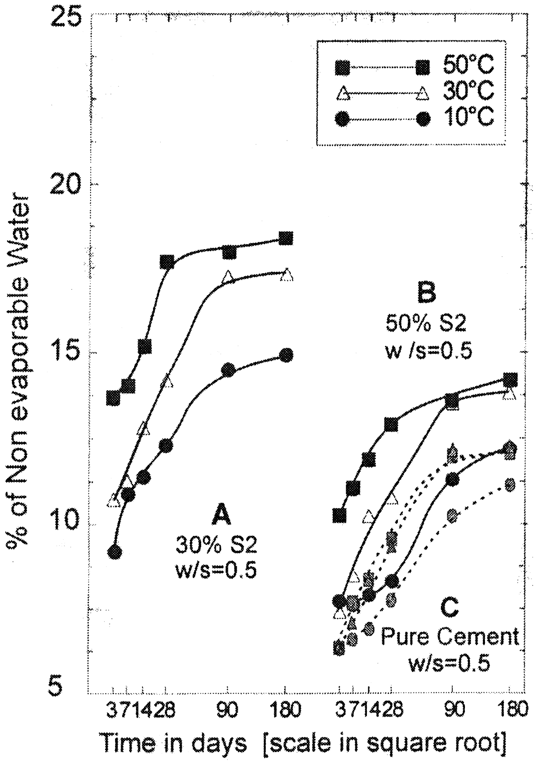

Fig. 5. NEW versus time for blends of cement with slag S2.

the slag S1 (higher vitreous fraction) displayed higher reactivity than S2 (lower vitreous fraction). After 180 days of hydration at 50°C, for 30% slag load, the percentage of slag reacted reached 50% for the cement with S1, whereas for slag S2 was only 20%. Even if the results of percentage of reacted slag were normalized with respect to the corresponding vitreous fraction, those of the slag S1 still indicated a higher reactivity. This difference is in agreement with various reports in the literature, in that higher vitreous fraction favors the slag reactivity [7,16,17], but in disagreement with a study on cements with slags 88–90% vitreous [18], which seems a rather narrow span compared to the vitreous fractions used in this study. It has to be considered that in the amorphous state there is a higher internal energy than in the crystalline state, which favors the reactivity of the slag.

3.2. NEW

NEW provides a semiquantitative indicator of the hydration of the cement, for blended cements, it contains the contribution of the cement and slag fractions, which cannot be separated. Figs. 4 and 5 present the results of NEW for both blended cements. There is a similar effect of the temperature as that observed for the percentage of reacted slag, an enhancement of the overall hydration of the blended cement. For a fixed w/s, it can be observed that as the slag load is reduced the amount of NEW was increased, compare curves A–B and C–D. It has been reported that the presence of the slag increases the reactivity of the cement fraction [5], and since the latter also reacts faster than the slag, as the cement fraction is increased more NEW can be expected. This effect was more marked for the cement with S2 (Fig. 5), in which the slag is less reactive hence contributing less to the NEW values.

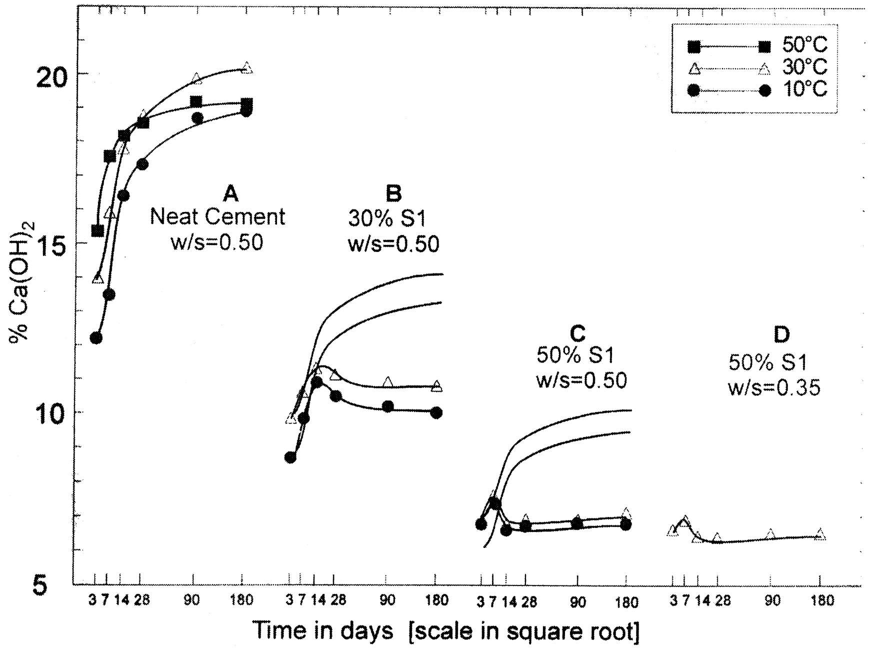

Fig. 6. Percentage of $Ca(OH)_2$ versus time for pure cement and blends with slag S1 hydrated under various conditions.

For comparison, Figs. 4 and 5 also included the nonevaporable from the neat cement normalized to 50% that corresponds to one of the levels of cement replacement by both slags. The two blended cements displayed higher NEW values than the neat cement, the effect was more marked in the cement with S1, similar results were observed at 30% slag replacement. This corroborates that the slags accelerate the cement hydration and also contribute to the NEW with their own hydration products.

3.3. Calcium hydroxide

Fig. 6 presents the results for the CH as a function of time for the cement with slag S1. The CH for the blended cements is presented together with the corresponding normalized curves of the neat cement. As the slag replacement level was increased, the amount of CH was reduced. For the first 7 days, the CH values of the neat and blended cements were similar, but after 14 days the amount of CH in the blended cements dropped slightly and changed very little from 28 days of hydration onwards, similar results have been previously reported [5,10,19]. This suggests that up to about 14 days the cement produces CH and the slag consumes it; since the cement hydration is enhanced in the presence of the slag, the CH values in the blended cement should be higher than those of the neat cement if the slag was not consuming CH. After 28 days, the cement has reduced its rate of reaction and the slag, which is still reacting, is consuming small amounts of CH for the formation of C–S–H products [20].

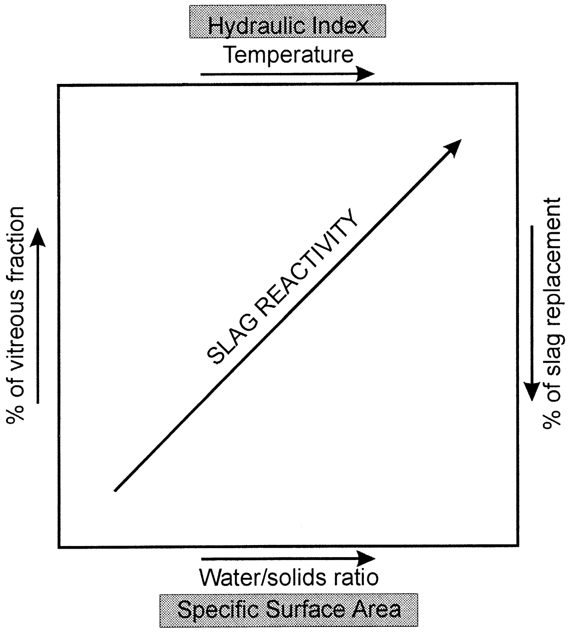

Fig. 7. Representation of the effect of hydration conditions and slag characteristics on the reactivity of slags. Shaded areas not covered in this study.

4. Conclusions

The reactivity of slag as a replacement of Portland cement was evaluated, under several hydration conditions, by means of a method of selective chemical dissolution. The overall reactivity of the blended cements was also assessed by means of NEW. It was found that higher hydration temperatures increased the reactivity of the slag, the NEW values observed a similar pattern. As the percentage of slag replacement was increased its reactivity was reduced, it was thought that this was a consequence of the reduction of the alkaline activating environment provided by the hydration of the cement. For increased amounts of water available for the reactions, the reactivity of the slag and the overall reactivity of the cement (amount of NEW) were increased. The slag with 97% vitreous fraction was more reactive than the slag with 53.5% vitreous fraction; even if the results of percentage of reacted slag were normalized with respect to the corresponding vitreous fraction, the former still appeared of higher reactivity. The general observations are summarized in Fig. 7, which includes the effects of the hydraulic index and the specific surface area, as reported in the literature, although not considered in this paper.

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