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COMPARISON OF REACTION DEGREES OF SLAG AND FLY ASH OBTAINED BY THERMOGRAVIMETRY AND SELECTIVE DISSOLUTION

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Abstract
The evolution of the reaction degree of supplementary cementitious materials (SCM) with time is an important aspect regarding the design and use of blended cements. However, this quantification is complex due to the multiple actions of SCM in the cementitious system, such as the filler effect, the consumption of CH and the formation of secondary calcium silicate hydrates. In this sense, different methods for the estimation of the reaction degree may be recommended for each type of SCM. Some of them are indirect methods that quantify hydration products and compute a reaction degree on that basis, e.g. thermogravimetric analysis, and others are direct methods that measure the amount of unreacted SCM, e.g. selective dissolution. In this paper, thermogravimetric analysis and selective dissolution are applied to estimate the reaction degree of cement pastes admixed with 40% slag or 30% fly ash. Curing periods ranged from 1 till 90 days. Results from both methods are compared and some comments on practicalities for their application are made. Although not enough evidence could be collected for any of the applied methods to be considered as a reference method, the simultaneous application of these two techniques offers increased reliability than when only one method is applied.

1. Introduction

The extent of the reaction of supplementary cementitious materials (SCM) in cementitious mixtures is a key question for the use of blended cement. Finding an answer for this question in not an easy task due to several reasons such as the reaction of clinker being affected by the "filler effect" from SCM, unreacted SCM being difficult to quantify due to its amorphous nature, and the reaction of SCM in cementitious materials being more complex and with a very probable different rate than in synthetic alkaline or lime saturated solutions [1].

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Different methods have been attempted for the quantification of the reaction of SCM in cementitious systems, and the convenience of one or another depends on the type of SCM in question. All methods have some drawbacks and at present there is no full agreement on a specific method for reference. Some methods are direct, in the sense that they attempt to quantify the amount of unreacted SCM in the sample (and thereby the amount of reacted SCM by difference with the original content); whereas other methods are indirect, as they quantify other phases in the microstructure that are produced or consumed during the reaction of the SCM (and by simplified computations a reaction degree of the SCM is obtained).

Selective dissolution (SD) of hardened samples is a direct quantification method that aims to dissolve all phases in the hardened sample but the unreacted SCM. Two of the most accepted methods use the EDTA+DEA+TEA solution for slag blends and the HCl+salicylic acid for fly ash blends [1]. Selective dissolution has received some criticism in relation with the actual selectivity of the dissolution [1]. In fact, the technique should be named "preferential dissolution", instead, as part of unreacted SCM is dissolved whereas parts of clinker and hydrates are undissolved at the same time. Moreover, possible precipitation of some compounds during drying should be added to the computation.

Several corrections have been proposed for more accurate results from SD. Lumley et al [2] suggested to correct undissolved fractions of slag blended mixes after EDTA dissolution for the formation of hydrotalcite-like phases, considering that the mass formed from the MgO in the reacted slag is $2.35 \times M$ (2.35 = mass hydrotalcite/mass MgO, and M = MgO content of the slag). This correction is still missing the amount of hydrotalcite-like phases that can be formed from dissolved cement, which will not be very significant if the MgO content of cement is low. It should be mentioned that this correction is based on the assumption that all MgO from dissolved slag contributes to precipitation of hydrotalcite-like phases, and this should still be experimentally quantified. Moreover, there is a fraction of undissolved alumina silicate hydrates [2], which should be also accounted for by a corresponding correction of the remaining fraction. Also for slag, in the CEN Standard [3] for anhydrous cements the values of residues are multiplied by 1.05 to account for dissolved unreacted slag. However, the actual amount of slag that dissolves varies significantly, and it is convenient to analyse the solubility of pure slag to make a more accurate correction. On the other hand, it might be alleged that this soluble fraction of slag is also the most reactive, and this correction would then not be necessary for advanced reaction degrees [1]. Finally, the acid solution used for fly ash blends is unable to dissolve some components of the Portland cement (mainly sulfate), and the residue should be analysed for its sulphate content (SO_3) and corrected accordingly. Vollpracht et al [4] demonstrated that sulphate bearing phases like ettringite or monosulfate in hydrated cement paste are in fact dissolved but, during drying, they precipitate later in different phases from the original, and this sulphate correction is then necessary.

Even with the corrections mentioned above, some studies claim that large, non-quantifiable systematic errors remain from different assumptions leading to large differences in the obtained reaction degrees for fly ash or slag reacted [5-6]. These inaccuracies are generally considered to result in an underestimation of the reaction degree in the order of 10% [1].

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Among indirect methods, evaluation of the bound water content from the weight loss of samples between 105° and 1000°C is the most widespread technique to assess the hydration degree of unblended Portland cements.

First, the overall reaction degree can be represented by the ratio of the bound water content at a certain time t (or maturity M if temperature is not constant) (w_b (t)), to the ultimate bound water content w_b (∞) [7]. Here, the value at infinity can be determined from a three parameter equation (Equation 1) that fits experimental data of w_b as a function of time [7], which is based on the one from Hansen and Pedersen [8] for describing strength development. This Equation has been also applied by [9] to calculate overall reaction degrees of OPC pastes and OPC pastes admixed with slag.

$$w_b = w_{b,\infty} \cdot exp\left[-\left(\frac{\tau}{t}\right)^a\right] \tag{1}$$

But the application of this technique for blended mixes is more complicated than for pure OPC pastes, as is it not possible to distinguish between the bound water involved in the reaction of the SCM and that involved in the reaction of the clinker phases. In fact, there is a change with time in the amount and chemical composition of hydrates in correspondence with products derived from hydration and from pozzolanic reaction [10]. Then, the only option seems to make a comparative analysis between blended mixes and unblended mixes that could help in the quantification or the reaction of the SCM on the basis of the differences.

In order to assess the reaction degree of SCMs, the consumption of portlandite (CH) can be considered. The reaction of SCM is separated from hydration of clinker by considering the consumption of CH in the blended mix that is compared to a reference unblended mix. This information is obtained from thermogravimetric analysis, with a quantification of CH from the weight loss in the range of 410-480ºC. The weight loss during CH dehydroxylation can be used to compute the amount of CH, considering the ratio between the molecular weights of CH and water. Based on the amount of CH in the mix, Pane and Hansen [7] developed a method to quantify the reaction of SCMs. The consumption of CH during its reaction is derived from different plots of the CH-content (per g OPC) versus w_b (per g OPC) for unblended and blended pastes. From this difference, Equation 2 allows the computation of the reaction of the SCM. Here, the reaction of the clinker might be accelerated and enhanced due to the filler effect of SCMs, and the comparison with a mix blended with an inert filler as reference instead of a plain unblended mix has been suggested [1].

$$r_S\left(w_b(t)\right) = \frac{CH_{OPC}\left(w_b(t)\right) - CH_{blend}\left(w_b(t)\right)}{CH_{OPC}\left(w_b(\infty)\right) - CH_{blend}\left(w_b(\infty)\right)} \tag{2}$$

A different approach considers simplified mass balance calculations to estimate the degree of reaction of SCM based on the CH consumption [11]. However, there are some variations in the composition of C-S-H that might result in unreal estimations if an erroneous Ca/Si ratio is considered. Appropriate values for the Ca/Si ratio are difficult to be obtained given the variability of this phase in hardened pastes [12]. The presence of an SCM leads to a decrease

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of the Ca/Si ratio of the C-S-H even in the presence of CH [11-13]. This indicates that some calcium for the pozzolanic reaction is coming from the C-S-H, and that the value of the Ca/Si ratio is dependent on the reaction degree of the SCM itself. A serious underestimation of the degree of reaction of the SCM results if only the CH consumption is considered.

Given the mentioned drawbacks of quantification methods for the reaction degrees of SCMs, it seems convenient that multiple methods are applied for increased reliability. Then, the impact of unresolved variables is reduced.

In this paper, two methods for the determination of the reaction degree of slag and fly ash in cement pastes are compared: selective dissolution (SD) and thermogravimetry (TG). Samples with two slags and two fly ashes were prepared and hydrated for up to 90 days. Then, hydration was stopped and the reaction degree was estimated by the aforementioned methods.

This paper presents the results obtained at Ghent University during a Round Robin Test on methods for quantification of reaction degrees of SCMs, carried out within RILEM TC 238-SCM, Working Group 2.

2. Experimental

2.1 Materials

Two ground granulated blast furnace slags (S1 and S2) and two fly ashes (F1, calcareous, and F2, siliceous) were analysed. Cement pastes with ordinary Portland cement (PC) and replacement ratios of 40% for slag or 30% for fly ash were prepared and seal cured for 1, 7, 28 and 90 days. Reference pastes blended with 30 and 40% quartz (Q) were also prepared. The w/b was 0.40. Properties of raw materials are presented in Table 1.

Table 1. Physical and chemical properties of raw materials.

	Chemical composition (%)								Particle size distribution (μm)		
	Al_2O_3	SiO_2	CaO	Na_2O	K_2O	MgO	Fe_2O_3	SO_3	d10	d50	d90
S1	11.6	36.5	40.8	0.5		7.5	1.4	2.1	3.1	18.3	42.5
S2	11.6	36.7	38.9	0.2	0.7	7.8	0.5	2.8	1.1	8.0	30.8
F1	19.8	42.3	20.7	0.3	1.5	2.2	8.2	1.4	1.7	10.0	30.8
F2	24.4	70.8	0.1	0.1	0.6	0.2	2.2	-	1.1	8.2	31.0
PC	5.7	19.3	63.7	0.2	1.2	1.6	3.6	3.2	1.2	13.0	49.9
Q	1.0	97.9	0.0	-	0.8	-	0.0	-	2.9	10.2	30.7

After curing, samples were cut into discs approximately 2-3mm thick and hydration was stopped by solvent exchange with isopropanol. Then, vacuum dried samples were stored under vacuum until tested. Soda lime was located in the vacuum chamber to prevent

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carbonation, and the outer layer of discs was pre-emptively disregarded for analyses due to the same reason. Analyses were performed on samples manually ground with mortar and pestle to particle sizes < 63 µm. Grinding was done immediately before testing.

2.2 Methodology
2.2.1 Selective dissolution (SD)
The methods followed were those described in CEN/TR 196-4 [3]. After dissolution, residues were collected by vacuum filtration in pre-dried glass fibre filters, washed and dried at 100 °C. Results are the average of triplicate determinations. For the computation of reaction degrees, the residues per 100 g of cement paste ignited at 1000 °C were considered.

For fly ash cement pastes, samples were treated with a solution of HCl + salicylic acid in methanol for 30 min. The procedure applied to the raw fly ashes resulted in residues of (79.48 ± 0.54)% and (99.68 ± 0.25)% for F1 and F2, respectively. The high solubility of F1 in association with its calcareous nature causes a high uncertainty for the computation of reaction degrees from residues of hydrated blended pastes. Therefore, only reaction degrees for F2 are presented. Moreover, the method applied for fly ash pastes results in sulfate bearing phases like ettringite or monosulphate, which are initially dissolved but precipitate later as gypsum, and during the drying of the residue bassanite is formed [4]. Therefore, corrections for sulphate contents were made. Sulphate contents of residues were determined by the combustion infrared detection technique. Reaction degrees for F2 were computed from Equation 3 derived from [4] and [14]. Where w_2 is the weight of residue [g], w_1 is the ignited weight of sample [g], w_{2o} is the weight of residue for pure OPC sample [g], w_{1o} is the ignited weight of pure OPC sample, $a/(a+b)$ is the content of SCM (a) to the total amount of cementitious material (a+b), $b/(a+b)$ is the content of OPC (b) to the total amount of cementitious material (a+b), w_a/a is the relative residue of the SCM, S_r is the SO_3 content of w_2 by weight, and S_{ro} is the SO_3 content of w_{2o} by weight.

$$\alpha = 1 - \frac{(1 - 1.813 \cdot Sr)\, w_2}{\frac{a}{a+b} \cdot w_1} - \left(1 - \frac{w_a}{a}\right) + \frac{\frac{b}{a+b}(1 - 1.813 \cdot Sro) \cdot w_{2o}}{\frac{a}{a+b} \cdot w_{1o}} \tag{3}$$

For slag cement pastes, samples were treated with EDTA+TEA+DEA solution for 120 ± 5 min. The procedure applied to the raw slags resulted in residues of (95.03 ± 0.14)% and (95.20 ± 0.73)% for S1 and S2, respectively. Reaction degrees for slag were computed from the Equation 4 [14], where no correction for hydrotalcite-like phases is considered. Where w_2 is the weight of residue [g], w_1 is the ignited weight of sample [g], $a/(a+b)$ is the content of SCM (a) to the total amount of cementitious material (a+b), $b/(a+b)$ is the content of OPC (b) to the total amount of cementitious material (a+b), w_a/a is the relative residue of the SCM, and w_b/b is the relative residue of the OPC.

$$\alpha = 1 - \frac{w_2 + \frac{a}{a+b} \cdot \left(1 - \frac{w_a}{a}\right) \cdot w_1 - \frac{b}{a+b} \cdot \left(\frac{w_b}{b}\right) \cdot w_1}{\frac{a}{a+b} \cdot w_1} \tag{4}$$

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2.2.2 Thermogravimetry (TG)

Samples of approximately 50 mg were exposed under an inert atmosphere of nitrogen to increasing temperatures, ranging from 20 °C to 1100 °C at a rate of 10 °C/min. Reaction degrees were computed following the procedure according to Pane and Hansen [7], by which CH consumption by the pozzolanic reaction is computed from the difference in the CH-bound water relationship between the blended cement paste and the non-blended cement paste. The tangential method was used for determination of the water loss due to CH dehydroxylation. For TG computations, the correction for the calcite content in the samples was disregarded, as the loss at this temperature range might be due to some interlayer isopropanol. Bound water was computed from the weight loss between 105-1000 ºC.

3. Results and Discussion

Figure 1 shows the relationship between bound water and CH contents obtained by TG for the different pastes. The effect of the filler effect on this relationship seems slight, pastes with 30 and 40% of quartz (Q30 and Q40) show little higher values of CH content than those for the unblended paste (PC) around 20% of bound water content, but fitting the three series together results in little differences from separate fittings. Instead, Q30 and Q40 show simultaneous higher values than PC for both bound water and CH contents. This is to be expected, as the filler effect causes an enhancement of hydration, but there is no mechanism of CH consumption involved, and in consequence the relationship between the chemically bound water and this hydration product should remain the same. This consideration is not valid if the comparison is made for the same curing period, as the progress of hydration is sensible to filler effect. Therefore, if the same value for $w_b(t)$ is considered for the unblended and blended pastes, i.e. the comparison is made on the basis of equivalent hydration degree and not equivalent curing time, any influence of filler effect is avoided (as shown in Figure 1).
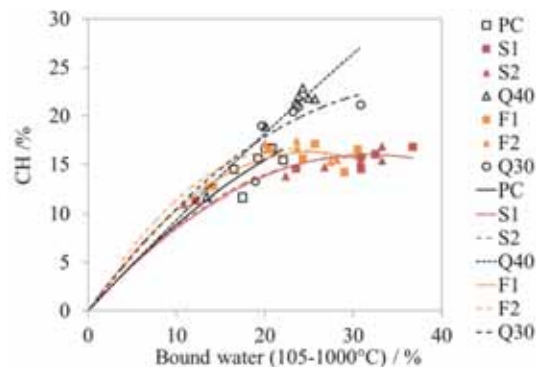

Figure 1. Bound water versus CH content for the pastes.

Moreover, there is no clear distinction between both types of slags, and what is more, neither between both types of fly ash (even when one was calcareous and the other siliceous). This could suggest that a general correlation may be proposed for each type of SCM, and further research in this regard seems interesting.

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The fittings in accordance with Equation 1 for the evolution of bound water content are shown in Figure 2, where fair correlations can be seen however additional data for longer curing periods would be necessary for full validation of the three fitted parameters. Still, the obtained results are consistent with the model from Equation 1 and bias seems independent of the curing period. A particular issue for fly ashes is that bound water seems to increase linearly with the logarithm of time, and very high values for the ultimate bound water content were obtained (64.3 and 46.8 % for F1 and F2, respectively) in comparison with the values for slags which seem more realistic (37.5 and 35.3 % for S1 and S2, respectively). These rather unreal values for the fly ashes are a result of their very slow reaction rate, and more extended curing periods must be investigated for improved results. Then, the method by Pane and Hansen [7] as it is, seems more appropriate to be used for computation of the reaction degree of slag than fly ash blended pastes.
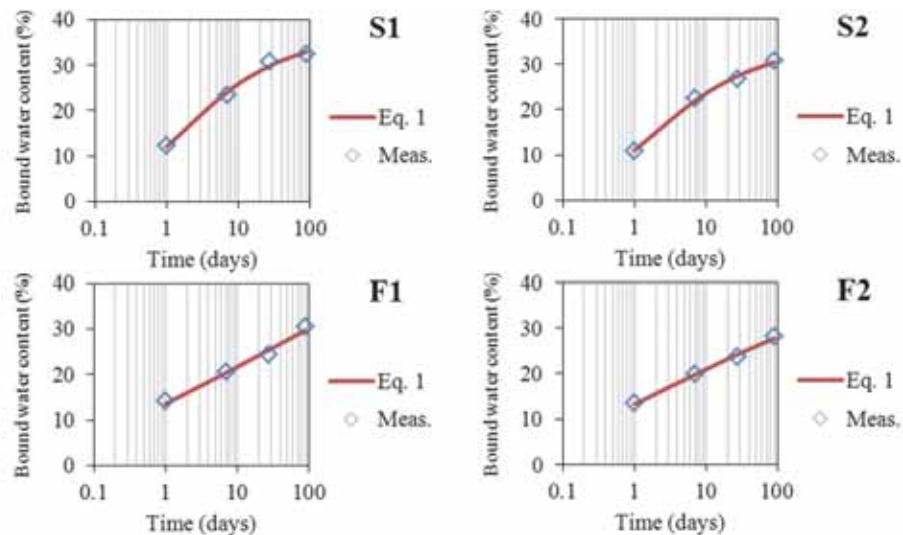

Figure 2. Bound water in blended cement pastes, measured values versus estimated values from (1) [7-8].

The reaction degrees of slag and fly ash, determined by means of SD and TG, are presented in Figures 3 and 4, respectively. From the comparison of the reaction degrees obtained by the applied methods, it can be seen that the differences are within the estimated precision ranges reported in [1] for these methods. Results from the SD method consistently resulted in lower values than results from TG.

For the case of slags, the lower values for the reaction degrees obtained by the SD method are only partially due to no correction for the undissolved hydrotalcite-like phases being made. Additionally, the computation in Equation 2 considers that the dissolved fraction of raw SCM is completely unreactive, and it is then discounted for the reaction degree. However, it is very likely that being this fraction the most soluble under chemical attack, it is also the most

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reactive in the cement paste. Then, this correction would lead to inaccurate values for later curing periods due to the consideration of the soluble fraction as non-reactive. This consideration is also valid for the siliceous fly ash but as the soluble fraction of this raw material is much lower (0.32% for F2 vs. 4.97 and 4.80% for S1 and S2, respectively), the impact on the result is much lower. Finally, it should be mentioned that in the method based on TG the reaction degree is defined as the reaction at a certain moment relative to the maximum reaction that is possible (at infinity). This does not necessarily correspond with complete reaction of SCM, but with the maximum bound water content that the blend may reach. Differently, for the computation from SD, the reacted SCM (obtained by difference on the basis of the residual SCM) is compared with the initial amount of SCM. Then, whereas the SD method computes the reaction degree relative to the total amount of SCM, the TG method computes the reaction degree relative to the maximum reacting SCM.
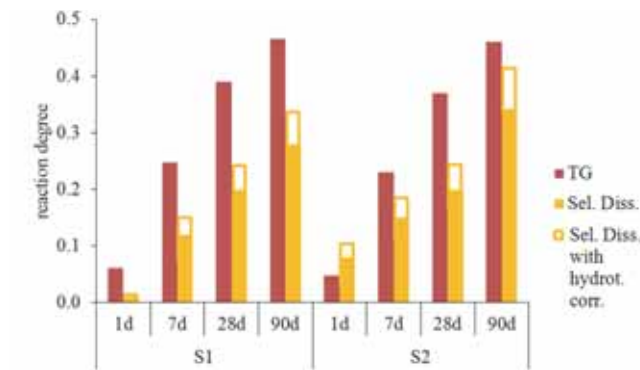

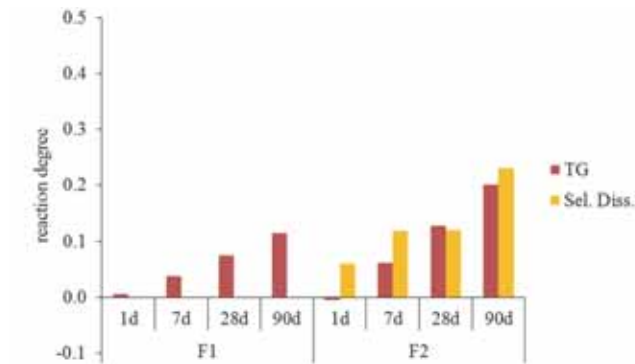Figure 3. Reaction degrees for slags.

Figure 4. Reaction degrees for fly ashes.

In this sense, when reaction degrees are corrected by the hydrotalcite-like phases formed from the reacted slag, increases of 21.4 and 22.4% are obtained for reaction degrees of S1 and S2, respectively (in accordance with the correspondent MgO content of slag that reacted and assuming a value for the stoichiometric coefficient of 2.35). Then, values are more similar but still lower than those obtained by TG. However, the correction by hydrotalcite-like phases is

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not accurate if the proportion of this phase in the residue is not further investigated, as the assumption of all dissolved MgO favouring the formation of precipitated products should be experimentally demonstrated. Then, even when this correction favours the consistency of results, its basis should be further investigated for appropriate correction coefficients.

More similar values were obtained for F2, where corrections for precipitated bassanite computed from SO_3 contents of the residues have been applied.

When the relative differences between the two quantification methods (i.e., $|\alpha_{TG}-\alpha_{sel.diss}|/(0.5 \cdot (\alpha_{TG}+\alpha_{sel.diss}))$) for the different curing periods are analysed (Figure 5), high values for 1 day for the three blends (S1, S2 and F2), and no significant variation between 7, 28 and 90 days, are observed. It should be noted that corrections due to the hydrotalcite-like phases contents of residues from slag blends are not considered in this comparison. The origin of these differences seems to be a systematic error that is rather independent from the value for the reaction degree. Then, the relative difference seems higher for 1 day only due to the small value of the reaction degree.
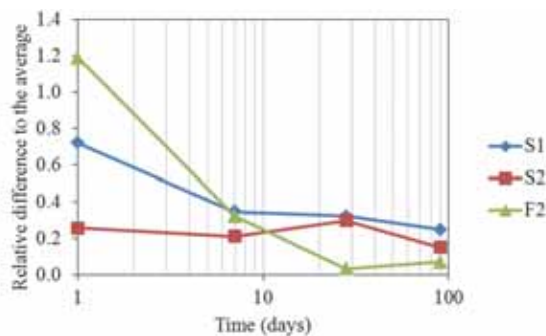

Figure 5. Evolution with time of relative difference between TG/SD and the average of both.

4. Conclusions

Reaction degrees of slag and fly ash were measured by SD and TG on blended cement pastes for curing periods between 1 and 90 days, the following conclusions are derived from the results:

- The method based on the ultimate bound water content and portlandite consumption applied for the analysis of TG data seems appropriate for slag, but some conceptual inconsistencies were obtained when applied for fly ash. This is in connection with the different reaction rate of each SCM. More research on reaction of fly ash is necessary, involving extended curing periods to obtain more realistic ultimate bound water contents.
- For the SD method, correction of reaction degrees of slag due to formation of hydrotalcite-like phases is convenient to avoid systematic underestimation. However, composition of the residues must be investigated for hydrotalcite-like phases contents in order to apply correct coefficients.

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− Results illustrate the accuracy of both methods. Given that there is no reference method for comparison at present, the simultaneous application of both methods offers an increased reliability of the values obtained for the reaction degree, with special consideration of the practical nature of these two methods when applied for this purpose.

Acknowledgments

References

[1] Scrivener, K. et al, TC 238-SCM: hydration and microstructure of concrete with SCMs, State of the art on methods to determine degree of reaction of SCMs, Mater Struct 48 (2015), 835-862.

[2] Lumley, J. S. et al, Degrees of reaction of the slag in some blends with Portland cement, Cem Concr Res 26 (1996), 139-151.

[3] CEN/TR 196-4 Methods of testing cement - Part 4: Quantitative determination of constituents (2007)

[4] Vollpracht, A. and Brameshuber, W.Investigations on then years old hardened cement paste samples, International RILEM Conference on Material Science, Germany (2010), Vol. III, 79-91.

[5] Ben Haha, M. et al, Quantification of the degree of reaction of fly ash, Cem Concr Res 40 (2010), 1620-1629.

[6] Kocaba, V. et al, Methods for determination of degree of reaction of slag in blended cement pastes., Cem Concr Res 42 (2012), 511–525.

[7] Pane, I. and Hansen, W., Investigation of blended cement hydration by isothermal calorimetry and thermal analysis, Cem Concr Res 35 (2005), 1155-1164.

[8] Hansen, P.F., Pedersen, E.J., Concrete casting in the winter (*Vinterstøbning af beton*), SBI-recommendation, 125, 1982 (in Danish).

[9] Gruyaert, E. Effect of blast-furnace slag as cement replacement on hydration, microstructure, strength and durability of concrete. PhD thesis, Ghent University (2011)

[10] Massazza, F. Pozzolana and Pozzolanic cements. [aut. libro] Massazza. [ed.] Arnold P.C. Hewlett. Lea's Chenistry of Cement and Concrete. 3rd. 1998.

[11] Antoni, M. et al, Cement substitution by a combination of metakaolin and limestone, Cem Concr Res, Vol. 42 (2012), 1579–1589.

[12] Deschner, F. et al, Hydration of a Portland cement with high replacement by siliceous fly ash., Cem Concr Res 42 (2012), 1389-1400.

[13] Lothenbach, B. et al, Supplementary cementitious materials, Cem Concr Res 41 (2011), 217-229.

[14] Luke, K. and Glasser, F.P., Selective dissolution of hydrated blast furnace slag cements, Cem Concr Res 17 (1987), 273-282.