

## **INFLUENCE OF PARTICLE SIZE DISTRIBUTION OF SLAG, LIMESTONE AND FLY ASH ON EARLY HYDRATION OF CEMENT ASSESSED BY ISOTHERMAL CALORIMETRY**

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### **Abstract**

Supplementary cementitious materials (SCMs) enhance early hydration of cement through the provision of nucleation sites for the precipitation of hydration products. This effect contrasts with the dilution effect of the mineral addition to the cementitious system. In fact, the net effect on heat release during the first hours of hydration is the reduction of peak intensity. Then, only when the specific heat is evaluated in terms of cement weight the actual effect of the admixture on hydration may be assessed. In this sense, a clear difference may be expected in accordance with the replacement ratio and fineness of the SCM. Increased specific surface favors nucleation and it therefore enhances hydration. In this paper, cement pastes admixed with slag, limestone and fly ash in three different fineness levels and three replacing ratios were investigated through isothermal calorimetry. The filler effect of each SCM was in relation with the fineness and replacing ratio, with higher impact on the aluminate reaction than on the silicate reaction of cement.

### **1. Introduction**

The hydration reaction of cement is an exothermic process. The total heat released during hydration is a function of the composition and relative amount of cementitious materials, and the water-cementitious ratio of the mixture. Isothermal (conduction) calorimetry allows continuous measurements of the progression of hydration at early ages, when the heat production rate is high.

Most supplementary cementitious materials (SCMs) in hardening cementitious materials become active after a few days, when the alkalinity is high enough, caused by cement hydration. It is usually considered that the amount of reaction of SCMs in the first few days is very often negligible and their influence is usually associated with filler effect. Two main mechanisms are generally acknowledged for contributing to the filler effect: extra space and enhanced nucleation. First, at the same water to solids ratio, the water to clinker ratio is higher

when part of it is replaced by SCMs and there is more space for the hydration products of the clinker phases. Secondly and particularly for fine materials, the extra surface provided by the SCMs provides nucleation sites for the precipitation of hydration products of clinker.

For example, the reaction of fly ash is slow at ambient temperatures, with marginal reaction degree up to 2 days [1]. Then, it contributes to increase the amount of portlandite compared to pure ordinary Portland cement (OPC) within the first days of hydration [2][3]. Subsequently, indications of fly ash reaction between 2 and 7 days are given by increased chemical shrinkage, bound water and reduced portlandite contents, with a consequential heat production by the SCM itself.

Even for slag, which is more reactive than fly ash, the amount of portlandite in slag blended systems remains similar or even higher (due to faster reaction of the clinkers caused by the filler effect) than in pure OPC systems during the first hours or days of hydration [2] [4], showing limited reactivity. However, Gruyaert [5] found that slag hydration already starts during the first days after mixing. Calorimetric measurements showed an extra hydration peak in the presence of slag and back-scattered electron (BSE) images indicated a slag hydration degree of 28% after 2 days for pastes with 50% of OPC replaced by slag. This early reaction might not be accompanied by portlandite consumption but it is indicated by heat production.

In fact, reactivity of a SCM and its contribution to heat production are connected. Whereas some authors report decreased cumulative heat with increasing slag content [6], others suggest in contrast that the long-term heat of hydration is higher when the mixes contain slag [2]. In the first case, the low amount of heat evolved is related with limitations in the reactivity and hydraulic index of the slag. Different values for the contribution of slag reaction to heat production can be found in the literature. Schindler and Folliard [7] indicated values for the maximum heat released at the end of the reaction of 461 J/g, whereas values of 355 and 440 J/g were reported in [8] and [9], respectively. On her part, Gruyaert [5] estimated the potential heat production of slag in the range of 400 – 500 J/g. These variations also seem to be due to different reactivities and chemical compositions. With increasing slag content, it is generally assumed that also the rate of heat evolution decreases [6,10], what would in the opposite direction indicate a filler effect that cannot compensate the dilution effect.

Limestone is commonly considered to have a pure filler effect. However limestone powder cannot be considered totally inert due to the formation of carboaluminates; the impact of these products on heat release and microstructure formation may be considered secondary [11].

Increasing the specific surface of the reactant can increase the reaction rate. But for SCMs the effect of reducing particle size is more complex due to the filler effect. Grinding is a common manufacture procedure for slag and limestone. Pal et al. [12] found a strong correlation between the hydraulic index of slags and Blaine fineness, together with chemical composition and glass content, at both 7 and 28 days. Swamy [13] reported that an increase in fineness of two to three times that of OPC can favor several engineering properties such as bleeding, setting time, heat evolution, high strength and durability. Thus, for better performance, the fineness of slag must be greater than that of cement.

Grinding is also an alternative processing method for increasing fineness and reactivity of a fly ash (although typical morphology of particles is substantially modified). Experimental results have confirmed that grinding not only increases fineness, but also reactivity, acid neutralization capacity and pozzolanicity of fly ash [14].

Blended cements are usually produced by intergrinding cement clinker with SCMs. But differences in hardness of the constituents tend to accumulate the SCM in certain size

fractions. For the particular case of slag, which is the hardest component, it tends to accumulate in coarse-size fractions. This results in less reactivity of slag and a reduction in strength that must be compensated by grinding the mix to an even finer degree. The advantages of grinding clinker and slag separately and mix them in appropriate proportions, such as lower specific energy consumption, ease of manufacture, higher addition of slag, and higher flexibility in product quality arrangements [15], result in this frequent production practice in cement plants. Also interground limestone blended cements are usually considered bimodal in terms of particle size distribution due to different hardness of limestone and clinker. But in this case, limestone is the softer material, and it is finer than clinker particles in the cement. Then, limestone is more favoured than slag to produce filler effect to enhance hydration of interground cements.

This paper deals with the enhancement of cement hydration allowed by slag, limestone and fly ash in different fineness degrees and replacement levels. Through isothermal calorimetry, the quantification of the enhancement of cement hydration due to the heterogeneous nucleation effect at short hydration times up to 7 days was investigated.

## 2. Assessment of heat production and hydration degree

The heat of hydration of cement at complete hydration ( $H_{cem}$ ) can be estimated from the weighted contribution of its constituents (Equation 1) [7]. Here,  $H_{cem}$  = total heat of hydration of the cement (J/g), and  $p_i$  = weight ratio of  $i$ -th compound in terms of total cement content.

$$H_{cem} = 500p_{C_3S} + 260p_{C_2S} + 866p_{C_3A} + 420p_{C_4AF} + 624p_{SO_3} + 1186p_{FreeCaO} + 850p_{MgO} \quad (1)$$

However, for blended systems, limited and varying data for the heat contribution of fly ash or slag can be found in literature. Some recommended values are 209 J/g [8] for fly ash and 461 J/g [8], 355-440 J/g [9], and 400-500 J/g [5] for slag. Limestone is usually considered as a non contributor to heat release itself [16].

Then, considering the relative cementitious materials content, the potential heat of hydration per unit weight of all the cementitious materials ( $H_u$ ) at complete hydration is computed from Equation 2. Here,  $p_{cem}$  = cement weight ratio to total cementitious content,  $p_{SCM}$  = SCM weight ratio to the total cementitious content, and  $h_{SCM}$  = heat of hydration of SCM (J/g).

The heat produced at a time  $t$  divided by the total heat available provides a measure of the progress of hydration [17] (Equation 3), as a simplified indirect method of estimating the overall degree of hydration (it assumes a single value for the hydration degree for the mix of all clinker phases and slag) of the cementitious system. Where,  $\alpha(t)$  = degree of hydration at time  $t$ , and  $H(t)$  = cumulative heat of hydration released at time  $t$ , (J/g).

On the basis of the experimental determination of heat production during hydration, a best fit mathematical model has been suggested [18]. The s-shape of the hydration development can be accurately represented by the exponential formulation in Equation 4. Where,  $Q(t)$  = the cumulative heat production at time  $t$ ,  $\tau$  = hydration time parameter (hours),  $a$  = hydration shape parameter, and  $Q_\infty$  = cumulative heat released after complete hydration.

From experimental data, values for  $Q_\infty$  lower than the potential long-term heat production,  $H_u$ , have been obtained [5], mainly due to practical unfeasibility of achieving complete hydration at ambient temperature in accordance with the Mills equation (Equation 5) [19].

$$H_u = H_{cem} \cdot p_{cem} + h_{SCM} \cdot p_{SCM} \quad (2) \quad \alpha(t) = \frac{H(t)}{H_u} \quad (3)$$

$$Q(t) = Q_\infty \cdot \exp\left(-\left[\frac{\tau}{t}\right]^\alpha\right) \quad (4) \quad \alpha_u = \frac{1.031 \cdot w/c}{0.194 + w/c} \quad (5)$$

### 3. Materials and Methods

Two types of slag (SA and SB), one limestone (LA) and one fly ash (FB) were analysed in this study. Mineralogical and chemical compositions of raw materials are presented in Tables 1 and 2, respectively. Amorphous contents of slags and fly ash were determined by the Rietveld analysis of XRD with internal standard. Grinding in a laboratory ball mill was applied for obtaining three fineness levels. Particle size distributions measured by laser diffractometry are shown in Table 3. Each ground material is identified with increasing numbers (1 to 3) for increasing fineness.

With these materials pastes were prepared with a w/b ratio of 0.45 and replacement ratios of cement by SCM of 20, 40 and 60% for slag, 10, 20 and 30% for limestone and 20, 30 and 40% for fly ash. These pastes were manually mixed and immediately introduced in a conduction calorimeter for the determination of heat production under isothermal conditions at 20 °C. Measurements up to 150 h of hydration were obtained.

Table 1. Mineralogical composition of raw materials by XRD/Rietveld analysis (%).

Material	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Anhydrite	Quartz	Magnetite	Calcite	Amorphous
OPC	60.2	22.0	10.8	2.7	4.2	nd	nd	nd	nd
LA	nd	nd	nd	nd	nd	10.0	nd	75.2	nd
FB	nd	nd	nd	nd	nd	5.9	1.2	nd	91.9
SA	nd	nd	nd	nd	nd	0.4	nd	nd	99.6
SB	nd	nd	nd	nd	nd	1.2	nd	nd	98.8

nd: below detection limit.

Table 2. XRF chemical compositions of raw materials (%).

Material	LOI	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	Free CaO <sup>(1)</sup>
OPC	1.80	0.27	0.95	4.91	20.74	2.96	0.77	64.67	1.52	0.2
LA	37.29	1.25	1.41	1.28	8.15	0.05	0.28	48.45	0.88	0.5
FB	1.84	1.08	1.92	23.50	54.19	0.94	3.38	3.02	7.92	0.1
SA	nd	1.91	12.14	8.62	28.89	1.85	0.43	36.16	0.95	nd
SB	nd	0.35	8.18	11.36	33.70	0.03	0.34	38.34	0.43	nd

nd: not determined.

(1) determined by titration

Table 3. Particle size distribution of OPC and SCMs ( $\mu\text{m}$ ).

Mat.	OPC	LA1	LA2	LA3	FB1	FB2	FB3	SA1	SA2	SA3	SB1	SB2	SB3
d10	3.1	2.5	2.2	1.6	2.1	1.7	1.4	1	0.8	0.9	2.2	1.8	1.3
d50	16.3	9.5	4.9	4.3	15	11	7.5	7.7	6.6	5.7	12.4	11	7.6
d90	57.9	76.4	51.1	26.7	89.3	44.7	25.2	56.7	58.4	25.8	32.1	32.9	32

Before mixing, the components were thermally conditioned at 20 °C to equilibrate them with the isothermal environment. As the components were manually mixed together and put outside the calorimeter, the first heat peak could not be registered completely and the integration of heat was done starting 30 min after contact between cement and water.

#### 4. Results and Discussion

The evolutions of heat production for blended pastes are presented in Figures 1. Also results for paste made with OPC only (P) with the same water/binder ratio is presented for reference.

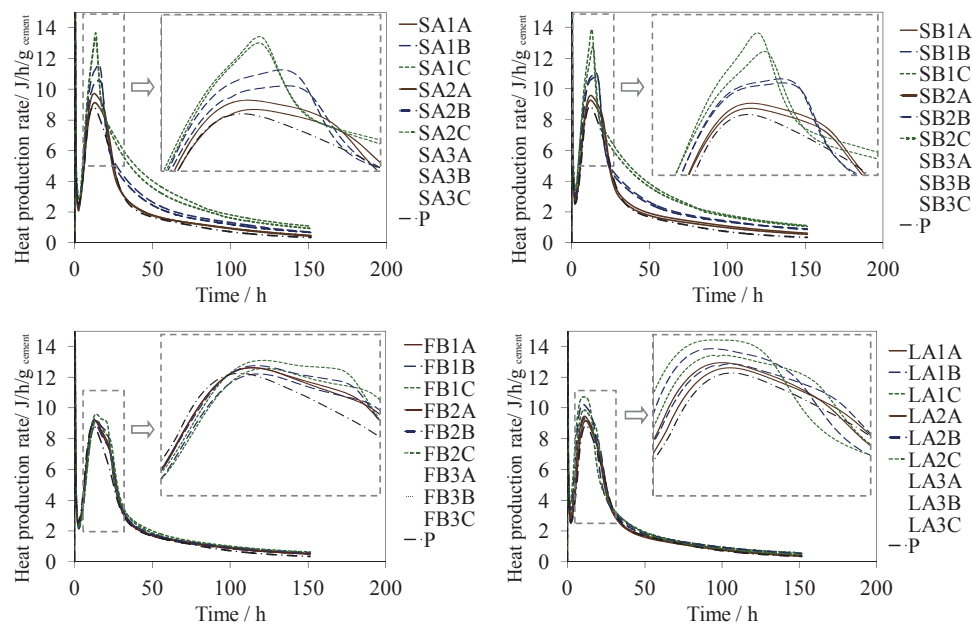


Figure 1. Heat production rate during hydration of pastes (for each SCM, A/B/C pastes indicate increasing replacement ratio, 20/40/60, 10/20/10 or 20/40/60%, respectively for slag, limestone and fly ash). Magnified frames show results for the first 24 h.

Both slags show the same trend with quantitative differences only. The increase in heat evolution during the acceleration period is steeper with higher replacing ratio and fineness. This acceleration period is associated with the accelerated formation rate of C–S–H. Also the maximum heat flow is higher, and the deceleration period steeper. This is consistent with an increase in the number of nucleation sites for enhanced cement hydration. Despite the heat maxima for slag blends increase in relation with the unblended reference, the rates of heat release decrease faster than for the reference and after approximately 24 h of hydration the difference among the curves (including the reference) is significantly reduced. Subsequently, heat release rate beyond 24h is increased with increasing fineness due to further enhancement of cement hydration and possibly also due to slag reaction on the basis of its higher specific surface and an earlier activation caused by higher amounts of portlandite release in the first hours. Then, for the case of the finest slags, their influence on the reaction rate seems not totally explained by the filler effect only, and also reaction may be considered.

Moreover, there is a shift in the heat maximum for both slags when the replacement ratio is higher and the SCM is finer. For the reference sample the heat maximum corresponds to the enhancement of  $C_3S$  hydration, whereas a very smooth shoulder can be observed in correlation to  $C_3A$  reaction after the depletion of the calcium sulphate phases [10,20–22].

For the blended mixes, this shoulder is related to the filler effect and connected with the fineness of the blends [16]. The effect becomes more noticeable with increasing content, and for 40% of slag it already becomes a third peak that exceeds the one corresponding to the silicate reaction and becomes the heat maximum itself. For 60% replacement this shift is extreme and it is difficult to notice the contribution of the silicate reaction. This change is not only quantitative, as also earlier times for the heat maximum were obtained with increasing replacing ratios and fineness levels. This is obvious when the heat maximum corresponds to a different reaction, but it is also noticed when comparing blended pastes with 40 and 60% of slag, where earlier times for the heat maximum are also noticed.

Higher replacing ratios mean lower  $C_3A$  to react. If aluminate is the only responsible, then the total heat released by this phase should be lower as the dilution effect results in less  $C_3A$  content. The enhancement of  $C_3A$  reactions seems not to completely explain the higher heat maximum caused by slag. Lothenbach et al [23], on the basis of the work of Kocaba [4], suggested that this is due to fillers and SCMs promoting the nucleation of the hydrates forming during this aluminate reaction instead of reacting themselves, but results from the present study suggest that this effect is dependent on the reaction of slag in connection with its fineness and replacing ratio. Previously, similar effects on the aluminate peak have been reported for slag blends and attributed to an early reaction of the slag itself [24,25]. This seems to be supported by the values for cumulative heat (Figure 2), which show much higher values for slag blends than those corresponding to the cement in the mix.

Especially for fly ash blends, but also for limestone blends in a lower degree, it seems that nucleation effects may be even more marked in the case of the hydration products of the aluminate phase. The additions of these fine materials have a limited impact on the silicate reaction, but the relative impact on the aluminate reaction is much more significant. The aluminate peak is sharpened, becoming narrower and higher with increasing fineness and replacement ratio. This illustrates that the seeding effect of SCMs is affecting the aluminate reaction more than the silicate reaction. This is also supported by a study on blends with completely inert fillers [22].

Also limestone accelerates the OPC hydration as it is seen that there is an impact on the slope of the heat evolution curve during the acceleration period. The second peak appears slightly earlier with increasing limestone content and fineness level (Figure 1). This is not the case for fly ash, where the heat release is maintained or slightly delayed (Figure 1). This retarding effect of fly ash on the cement hydration is repeatedly reported in the literature [24][26].

The results indicate that the dilution effect from SCMs has an acceleration effect, but for the case of fly ash other factors are more important in the presence of this SCM.

The accelerating influence from SCMs depends on their specific surface for allowing heterogeneous nucleation. As the fineness of the SCMs becomes finer than that of cement, the contribution of heterogeneous nucleation towards the acceleration of the cement hydration is more noticeable.

However the acceleration period is not significantly modified, with the maximum heat evolution occurring a little earlier or more or less at the same time. An exception should be made for slags but this is due to a shift of the main reaction contributing to the maximum peak. This maximum corresponds to impingement of hydration products and growth controls the reaction kinetics beyond this heat peak [27]. The deceleration period starts when C-S-H grows out from the cement grains in a diffuse manner [28]. Then, the diffuse layer does not seem to affect the silicate reaction and C-S-H growing during the deceleration period, and enhancement of hydration by SCMs does not result in an extended thermal power. This might be attributed to the extra space that the SCMs allow, which compensates the higher amount of early hydration products. Moreover, for the particular case of limestone, it is seen that with increasing replacing ratio (up to at least 30%), hydration enhancement (i.e., provision of more nucleation sites) overcomes the dilution effect provided by additional space, and deceleration is then a little earlier due to greater diffusion control.

Figures 2 show decreasing cumulative heat production for pastes with increasing SCM content. However, this does not necessarily mean that the total heat production at time 'infinity' for pastes with slag is considerably lower than for the plain paste. The estimated values of  $Q_{\infty}$  obtained by fitting Equation 4 are shown in Figure 3. Only for replacement levels of 30% or more for limestone and fly ash the total heat production decreases considerably compared to that of OPC paste.

The effect of slag on  $Q_{\infty}$  is much less than that of limestone and fly ash, even more considering that higher replacement ratios have been applied for slags. This is caused by the reactivity of slags, which is much faster than that of fly ash, whereas limestone releases no heat at all. Moreover, for increasing fineness also  $Q_{\infty}$  increases. For the particular case of fly ash and limestone, little difference can be seen with a replacement ratio of 20%, but when this is increased to 30%, a significant decrease with the coarser fly ash is noted in comparison with the coarser limestone. For the case of slags, it is very remarkable that the release of heat due to reaction of slag plus the enhancement of cement hydration compensate the dilution effect of the SCM. In general terms, the heat release was reduced with replacing ratio only for the case of fly ash and in less extent for limestone.

Due to incomplete hydration,  $Q_{\infty}$  extrapolated from Equation 4 results in a lower value than that for the potential heat release,  $H_{cem}$  according to Equation 1 and composition in Tables 1 and 2 ( $Q_{\infty}=388$  and  $H_{cem}=492$  J/g for P). The ultimate hydration degree defined as  $Q_{\infty}/H_{cem}$  for P is 0.79, which is in between and agrees with values obtained by Gruyaert [5] for OPC (0.72-0.73 for  $w/c=0.40$  and 0.82-0.85 for  $w/c=0.50$ ). When  $H_u$  is computed for the blended

pastes, different ultimate hydration degrees for the different blends are obtained (Figure 4). Here, potential heat release values of 210 and 450 J/g were considered for fly ash and slag, respectively. For limestone, no heat release was considered. All the ultimate hydration degrees obtained are higher than the ultimate hydration ratio of Mills ( $1.03 \cdot w/b / (0.194 + w/b)$ ), 0.72 for  $w/b = 0.45$ , but some lower hydration degrees are obtained for the coarser SCMs in relation with the reference paste.

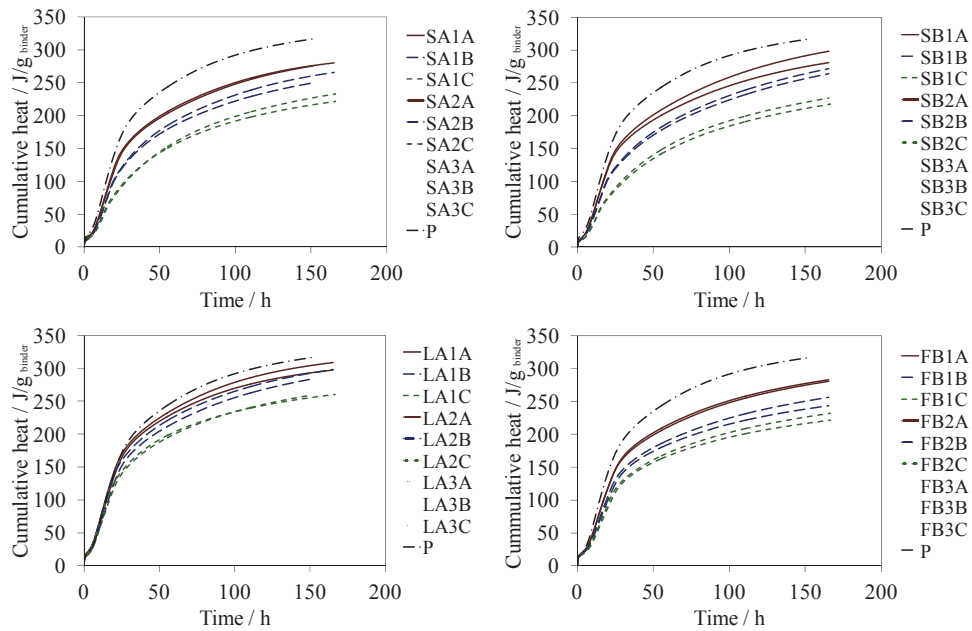


Figure 2. Effect of the SCM content on the cumulative heat production at early ages.

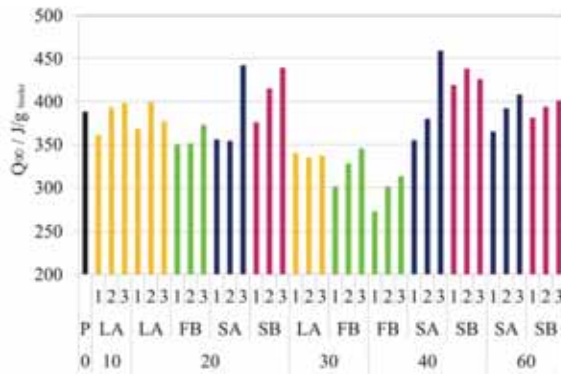


Figure 3. Effect of the SCM content on the long-term cumulative heat production.



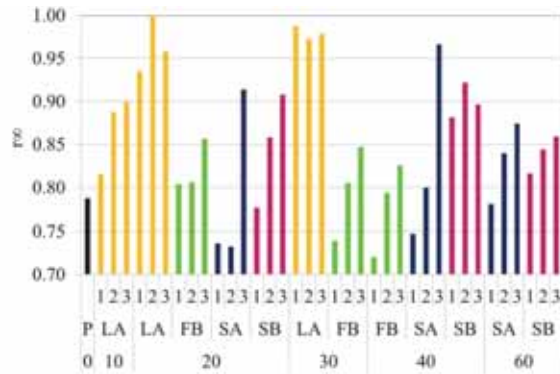


Figure 4. Long-term reaction degrees obtained from ultimate heat release and potential heat.

## 5. Conclusions

From the results of isothermal calorimetry of OPC blends with slag, limestone and fly ash, in three different fineness levels, the following is concluded:

- The filler effect of the three types of SCM showed higher impact on the aluminate reaction than on the silicate reaction of cement, and this effect was increased with the replacing ratio and fineness of the SCM.
- An acceleration of hydration was obtained with slag and limestone blending. This acceleration increased with replacing ratio and fineness. No acceleration was obtained with fly ash, and the effect was solely noticed on aluminate reaction.
- For the finest slags, the main peak shifted from the silicate reaction to the aluminate reaction, in connection with remarkable filler effect. However, increases in heat release cannot be completely explained with the filler effect, and considering the contribution of slag reaction itself seems necessary even as early as before 24 h of hydration.
- Increasing fineness of slag, fly ash and limestone showed a significant impact on hydration of cement, and the convenience of separate grinding that allows improved design of blended cements in which the SCM has a smaller particle size than clinker particles, with increased filler effect and reactivity, is shown.

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