

# Impact of filler on hydration kinetics

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## ABSTRACT

Quartz particles have been used to investigate the filler effect of slag in cement paste. The isothermal calorimetry data for quartz-cement paste when quartz has a similar specific surface area to slag particles were identical up to 24 hours. Over this period slag does not react chemically, however it enhances the acceleration period compare to plain cement. The surface factor seems involved in the controlling mechanism as quartz and slag with same particle size showed similar acceleration rate. After 1 day the slag reaction is dominant. The quartz-cement systems which simulate the filler contribution of slag, revealed that at long term the kinetics are mainly affected by the space available. Cement and blended systems with the same w/c ratio have a similar cumulative heat release at 28 days.

## 1. INTRODUCTION

In recent years the main route to lower the environmental impact of cement is the incorporation of increasing quantities of Supplementary Cementitious Materials (SCMs).

SCMs are able to substitute cement owing to their hydraulic and/or pozzolanic behaviour. These reactions occur simultaneously with cement hydration and they are interdependent this makes blended systems more complex than plain Portland cement. Measuring the reactivity of SCMs in blended systems becomes complicated. However the understanding of their reactivity is essential to optimize concrete and provide adequate properties.

There is a wide diversity of supplementary cementitious materials and the investigations on blended systems have been mainly focused on specific or local SCMs.

Consequently, today there is a lack of knowledge on the mechanisms in blended systems because we do not know the major parameters of these materials that affect the reaction kinetics. More often studies try to link chemical factors to the reactivity but there is usually an interaction of several factors (Scrivener and Nonat, 2011)

SCMs can be seen in two ways. They are reacting particles as they undergo chemical reactions and they provide chemical species from their dissolution. They are also grains or particles that can be describe by their morphology, size. Gutteridge (Gutteridge, 1990) identified that inert particles may influence cement hydration by enhancing the kinetics. This is usually known as a filler effect. So both chemical and physical aspects of SCMs contribute to the hydration kinetics of blended systems.

In this work is based we have investigated the impact of the filler effect by using quartz particles which are supposed to be inert. From these simpler systems without any chemical reaction from the particles, we have confirmed the existence of a filler effect in slag-cement paste. The period where the filler is dominant has been identified. And at long term when slag is reacting, the filler contribution has been studied.

## 2. MATERIALS AND METHODS

### 2.1. Materials

An ordinary Portland cement type Cem I, two slags and four quartz powders with different size grains have been used. The particle size distributions of the anhydrous materials have been determined by laser granulometry using a Malvern Mastersizer and are reported in Fig.1 .

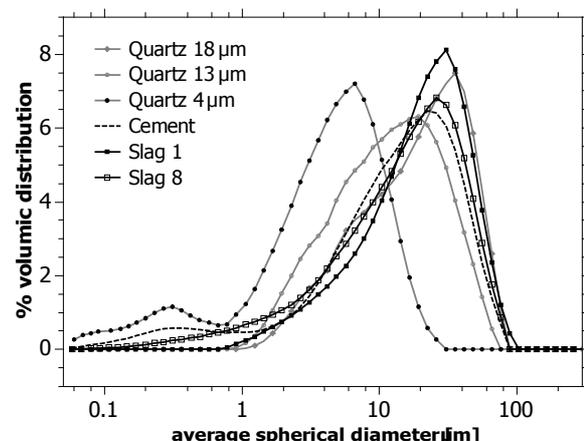


Figure 1: Particle size distribution of quartz powders, slag and cement

The specific surface area from the BET model for each material is also given in table 1. The specific surface area is defined as the area of solid surface per unit of mass. Actually is the accessible area of

solid surface per unit of mass. Thus, two particles with similar diameter can have a different S.S.A owing to the different roughness of their surface (i.e. Quartz 18 $\mu$ m and Slag1).

**Table 1.** Specific surface area of the materials used

Materials	Mean diameter ( $\mu$ m)	S.S.A ( $\text{cm}^2/\text{g}$ )
Cement	16	0.73
Quartz	18	0.79
Quartz	13	0.84
Quartz	4	4.86
Slag 1	18	0.87
Slag 8	15	0.9

## 2.2 Methods

Plain cement pastes with different quartz or slag substitution levels were prepared (10, 20, 40, 70%).

Prior to mixing with water, the anhydrous materials were mix together with a Turbula device to give good homogeneity. After addition of water the pastes were mixed for 2 minutes at 1600 rpm.

10 g of paste was used for calorimetry experiments. The heat flow was recorded by a TAM Air isothermal calorimeter at 20°C over 28 days.

The acceleration rate which occurs in range of 3h to 10 hours was estimated from the linear part of the curve.

## 3. RESULTS AND DISCUSSION

Fig. 2 shows the isothermal calorimetry curves for portland cement and blended systems, normalised relative to the Portland cement content. We observe that slag curve is very close to quartz 13  $\mu$ m. This is the quartz which has the nearest S.S.A. to the slag used. Over the acceleration period the two curves are superposed.

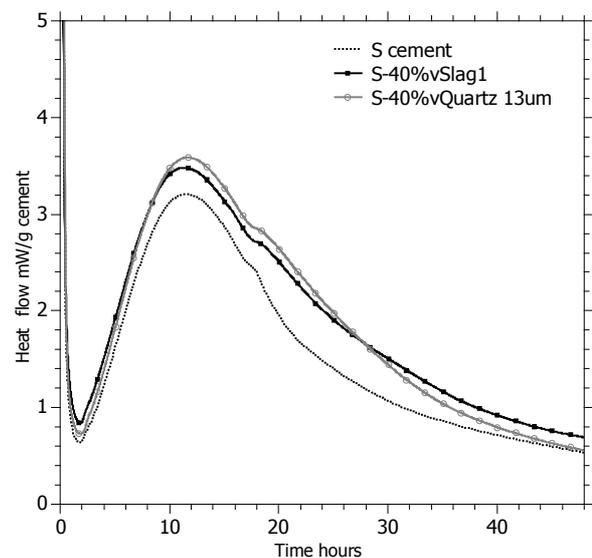
The volume of solids and water is the same in all the systems. As quartz and slag have a similar specific surface area, the overlapping between the two curves indicate that the surface factor is determinant over the acceleration period.

Many studies have reported a significant impact of increasing the surface as the surface of particles should act as nucleation sites for hydrates (Gutteridge, 1990; Stark, Möser et al., 2007). Nevertheless, the distance between particles which is drastically decreased when finer particles are used, could be also a reason.

The main variation between the quartz and slag curves occurs from 24 hours. At this time, the heat flow from slag system overtakes that of the quartz system and remains higher (Fig.2). The extra-heat

compare to quartz is coming from the reaction of slag itself. Thus, the crossing point would correspond to the beginning of slag 1 reaction.

The shoulder peak in the slow down of the curve corresponds to the depletion of solid gypsum (Hesse, Goetz-Neunhoeffer et al., 2011). In cement paste the main product formed at this time seems to be ettringite (Gallucci, Mathur et al., 2010). In slag-cement paste studies, this shoulder is enhanced and lot of authors (Wu, 1983; Escalante, 2004) presumed that it was due to the reaction of slag itself. However Fig. 2 clearly showed that quartz-cement produced the same effect on the shoulder as slag. Thus, the shoulder is only affected by the filler effect and this confirms the results from a previous study from Kocaba on slag-cement systems (Kocaba, 2009).

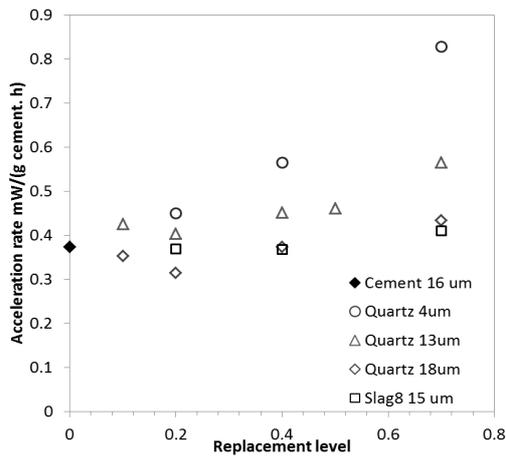


**Figure 2:** Isothermal calorimetry curves at 20°C of cement paste, 40%Quartz, 40%Slag (% volume)

The addition of mineral particles to cement grains has a significant accelerating effect (Fig 2). When quartz or slag is added in higher quantities, the effect is even more significant (Fig. 3).

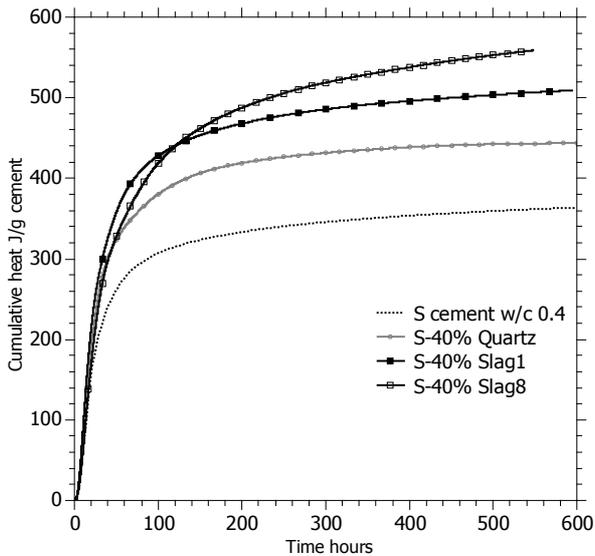
From the data of Fig. 3 the acceleration rate increases with fineness of the particles and with the replacement level. This is in good agreement with the surface factor influence that we already identified from Fig. 2.

It is also noticeable that the coarser fillers such as the slag 1 and quartz 18 $\mu$ m do not have a large influence on this rate.



**Figure 3:** Slope value of the acceleration period for different blended systems

From Fig.2 the reaction of slag started from 24h-28 hours. Actually slag still reacts after 28 days as we can see the constant increase of the cumulative heat with both slag-cement pastes in Fig.4. By subtraction with the quartz curve which represents the filler contribution of slag we can access to the own contribution of the slag reactivity. This method have been used by Kocaba et al. (Kocaba, 2012).

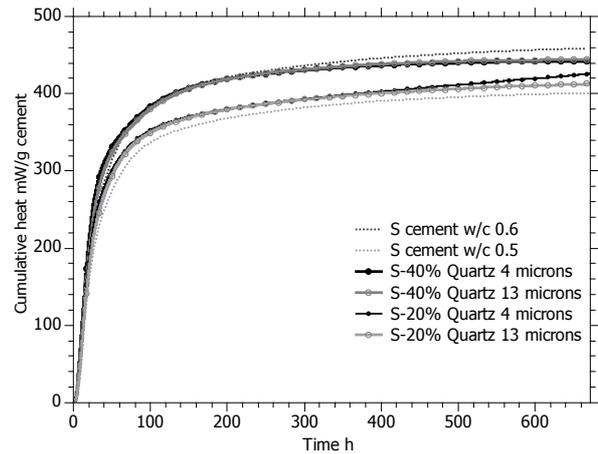


**Figure 4:** Cumulative heat monitored by isothermal calorimetry over 28 days.

Slag 1 and slag 8 have a specific surface area close to that of quartz 13µm. When finer quartz such as 4 µm is used, the cumulative heat is identical to that of quartz 13 µm (Fig. 5). This was found reproducible whatever the replacement level used. Although we observed in Fig. 2 finer quartz accelerates much more the main peak, at longer term it seems that the size or surface factor is not affecting the kinetics of hydration. To go further other experiments using coarse corundum with high S.S.A and rutile which is very fine (<1µm) were done at 40% of replacement. It results that even with different morphology and size, at long term the kinetics were similar for all the systems (i.e. quartz, corundum, rutile).

Thus, the dominant factor for later hydration would be the space available as all these systems present the same w/c ratio.

The curve of cement paste with water to cement ratio 0.6 confirm this assumptions. When 40% of cement is substituted by any filler in a paste with water/solids ratio 0.4 this corresponds to an effective water/cement ratio 0.66. In Fig. 5 curves of cement with w/c 0.6 and both quartz-cement curves of 40% substitution are joining at long term. Therefore, the later hydration would be dependant of the w/c ratio.



**Figure 5:** cumulative heat of quartz-cement paste with different size particles.

The water/cement ratio corresponds also to the water filled space. So, at later ages the kinetics would be controlled by the filling of the space remaining. Nevertheless, if we come back to Fig. 4 which illustrates the slag-cement heat, we notice that the cumulative heat is much higher than the quartz-cement with correspondent w/c ratio. This observation raises the question about the filling ability of the hydrates in slag-cement paste that have been highlighted recently (Scrivener and Nonat, 2011) with the evidence of different C-S-H morphology observed in slag-cement paste compare to cement paste (Richardson, 1999).

#### 4. CONCLUSIONS

The experimental results have established few keypoints as following:

- Quartz with similar S.S.A is able to simulate filler effect of slag.
- The acceleration period is significantly affected by a surface factor.
- The reactivity of slag starts around 24 hours in our case.
- Slag reaction has no influence on deceleration and on the shoulder peak except. So, the filler effect of slag is dominant over a period of 1 day.
- Fineness as well as the replacement level increase the acceleration rate. The

- interparticle distance or surface for nucleation would be the reason.
- At long term, quartz-cement system allow investigation of space filling.
  - w/c ratio has significant impact at long term that would means the late hydration would be controlled by the filling of space i.e the filling ability of the hydrates
  - Hydrates formed in slag-cement paste would fill the space in a different fashion compared to quartz-cement and cement paste.

## REFERENCES

- Escalante, 2004. The chemical composition and microstructure of hydration products in blended cements. *Cement and Concrete Research* 26: 967-976.
- Gallucci, Mathur, et al., 2010. Microstructural development of early age hydration shells around cement grains. *Cement and Concrete Research* 40: 4-13.
- Gutteridge, 1990. Filler cement: the effect of the secondary component on the hydration of portland cement. *Cement and Concrete Research* 20: 778-782.
- Hesse C., Goetz-Neunhoeffler F., et al., 2011. A new approach in quantitative in-situ XRD of cement pastes: Correlation of heat flow curves with early hydration reactions. *Cement and Concrete Research* 41: 123-128.
- Kocaba, 2009. Development and evaluation of methods to follow microstructural development of cementitious systems including slags. Lausanne, EPFL. Lausanne
- Kocaba, 2012. Methods for determination of degree of reaction of slag in blended cement pastes. *Cement and Concrete Research*. Submitted
- Richardson, 1999. The nature of C-S-H in hardened cements. *Cement and Concrete Research* 29: 1131-1147.
- Scrivener and Nonat, 2011. Hydration of cementitious materials, present and future. *Cement and Concrete Research* 41: 651-665.
- Stark J., Möser B., et al. (2007). Nucleation and growth of C-S-H phases on mineral admixtures  
*Advances in Construction Materials 2007*. C. U. Grosse, Springer Berlin Heidelberg: 531-538.
- Wu, 1983. Early stage hydration of slag cement. *Cement and Concrete Research* 13: 277-286.