# Hydration kinetics of cement paste with very fine inert mineral additives

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ABSTRACT: In the present paper results on the hydration kinetics of cement paste with small amounts of very fine filler additions are presented. In the first days of hydration very fine inert fillers show a distinct impact on hydration processes that exceeds the simple filler and dilution effect. The influence of the specific surface area, the mineralogical characteristics and the electric potential on the coagulation behavior and the distribution of the filler particles in the fresh suspensions are discussed. Hypotheses are presented to explain the influence of those parameters on hydration kinetics. Based on the results, suggestions are made for the realistic modeling of hydration kinetics of cement pastes with very fine inert fillers.

#### 1 INTRODUCTION

Inert fillers are frequently used for the enhancement of fresh and hardening concrete properties. Generally, fine particles fill out the pores between the cement particles, leading to a high particle packing / low initial porosity. Due to this "filler effect" hydration products have to bridge smaller gaps. Thus, with the same hydration product volume a denser microstructure is formed. The effect of inert fillers on rheology, hydration kinetics and porosity of cement paste and concrete depends on numerous parameters, such as fineness, grain shape, electric potential and other mineralogical characteristics.

For limestone powder it is known, that the amount of calcium carbonate and the total organic content have an impact on strength and water demand. Limestone particles usually accelerate early age hydration due to the "affinity" of the carbonate surfaces to hydration products. A part of the calcium carbonate reacts with the C<sub>3</sub>A from the cement, see e.g. Rahhal et al (2009). In contrast, crystalline quartz particles are inert and only act as fillers. Inert fillers with very high fineness show an improved filler effect, usually denoted as the "microfiller effect". The higher specific surfaces provide additional nucleation sites for hydration products. Consequently, the hydration rate is further increased and the initial porosity is decreased in comparison to fillers with normal fineness. The enhancement of the filler effect by finer grinding is limited. For very small particle diameters the interparticle forces become predominant, resulting in coagulations. Fillers with very high specific surfaces raise the water demand, and hence the initial porosity can increase. But the distinct rheological impact of very fine particles can be used for the design of concrete with "tailored" characteristics, as demonstrated by Budelmann and Krauss (2009).

For most technical tasks the consideration of inert fillers being chemically inactive and merely "diluting" cement pastes or concrete gives satisfactory results. This is particularly true for fillers with low or normal fineness and with regard to concrete properties at later ages. If the early age properties are of interest, such as setting, hydration kinetics and microstructure development,

this simple assumption is questionable. In order to enable realistic predictions of cement paste or concrete characteristics with different additives, more specific models are requisite. As an example Bentz (2006) incorporated the chemical reactions of limestone powder with  $C_3A$  into microstructure simulations. Other improvements of kinetic and microstructure models are suggested by Nehdi (1998). In the following new results are presented illustrating some special aspects of the impact of very fine inert fillers on hydration kinetics. The basic mechanisms are discussed and convenient model approaches are suggested.

## 2 EXPERIMENTAL

#### 2.1 Materials

For the calorimetry tests an ordinary Portland cement (OPC) CEM I 42.5 R after EN 197 with the following characteristics was used: specific surface area (Blaine) =  $3.440 \text{ cm}^2/\text{g}$ ,  $56.4\% \text{ C}_3\text{S}$ ,  $18.6\% \text{ C}_2\text{S}$ ,  $9.9\% \text{ C}_3\text{A}$ ,  $6.9\% \text{ C}_4\text{AF}$ ,  $0.7\% \text{ Na}_2\text{O}_{eq}$  and LOI (loss on ignition) = 1.3%. Silica fume (S1), two limestone powders (L1 and L2), two quartz powders (Q1 and Q2) and a natural clay powder (C1) were used as mineral additives. Some physical and chemical data are given in table 1. The clay powder consists of kaolinite, illite/muscovite and quartz. Long term reaction tests in OPC pore solutions at  $60^{\circ}\text{C}$  revealed no pozzolanic reactivity of the clay powder.

In figure 1 particle size distribution (PSD) curves from laser granulometry (LG) of the OPC and some additives are presented. The discrepancy between some of the LG d<sub>50</sub> values and the specific surface areas (BET) are partly attributed to particle agglomerations. By ultrasonic wave dispersion technique probably not all agglomerations were loosened. In addition the PSD curves are calculated assuming that particles have spherical grains. Therefore the error in the LG curves becomes greater for irregularly shaped grains. Very fine clay particles have got a plate-like shape with a much higher specific area / d<sub>50</sub> ratio than e.g. limestone or quartz particles. As Dur et al (2004) demonstrated, the clay particles are mainly encountered in the range < 2  $\mu$ m, whereas the more rounded quartz particles in the clay powder are found in the range > 0.8  $\mu$ m. Hence the error becomes substantial for clay powders, which was demonstrated by comparing LG data with TEM (Transmission Electron Microscopy) analysis results. Consequently, the PSD curves in figure 1 for the clay powder C1 but also for the micro quartz Q2 are unrealistic. Also specific surface areas obtained by the Blaine method exceeding 8,000 cm<sup>2</sup>/g have to be questioned. Because of that Blaine values for C1, Q2 and S1 aren't displayed here.

Pastes were produced with a constant water/solid (w/s) ratio of 0.40, while OPC was partly replaced by additives with replacement rates f = 0.05 and 0.10 (5 and 10 wt.-%). In this way a constant specific water content w<sub>0</sub> was given. Thereby, the total specific heat capacities of the pastes were about constant, resulting in more precise measurements. The change in the effective water/cement ratio (w/c)<sub>eff</sub> has to be respected for the interpretation of the results.



Figure 1. PSD curves for OPC and different fillers

Material	Silica fume S1	Lime- stone L1	Lime- stone L2	Quartz Q1	Quartz Q2	Clay Cl			
Chemical composition [m%]									
SiO <sub>2</sub>	98,3	6,5	6,5	99,0	98,5	68,0			
Al <sub>2</sub> O <sub>3</sub>	0,3	1,5	1,5	0,3	1,0	24,0			
CaCO <sub>3</sub>	-	90	90	-	-	-			
LOI	0,6	40,5	40,5	0,2	0,2	6,9			
Physical characteristics									
Density [g/cm <sup>3</sup> ]	2,20	2,70	2,70	2,65	2,65	2,69			
Spec. surf. area [cm <sup>2</sup> /g] (Blaine)	-	6.000	12.000	3.800	-	-			
Spec. surf. area [m <sup>2</sup> /g] (BET)	20,4	4,9	5,0	0,86	22,5	18,4			
d <sub>50</sub> [μm] (LG)	0,17	9,0	2,5	16,0	5,5	4,0			

Table 1. Chemical compositions and physical characteristics of the powders

## 2.2 Calorimetry tests and calculation of hydration degrees

All materials were stored at 20°C for 24 hours before the tests. The pastes were mixed with high intensity for 3 minutes. Superplasticizers were not used to exclude influences on hydration kinetics. The fresh pastes were stored in plastic containers in a water bath under sealed conditions directly in the calorimeter. The water temperature was kept constant at 20°C. After the measurements the specimens were stored at 40°C to ensure a high hydration degree. Subsequently they were cooled in the same calorimeter to the water temperature of 20°C to determine the heat transfer coefficient of each individual specimen. The tests were conducted in a self-built calorimeter as described by Nothnagel (2007). The greater specimen size and the insulation of the cylindrical plastic container provide semi-adiabatic conditions resulting in higher temperatures compared to isothermal conditions. By this setup the realistic hydration processes are reproduced better than in a pure isothermal calorimeter. Another advantage is that also concrete specimen can be tested in the same device, allowing good comparisons of results.

For the calculation of the hydration degrees from calorimetry the procedure described by Krauss and Budelmann (2010) was applied. The measured data were first corrected for the specific heat transfer coefficient. Then the adiabatic temperature rise  $\Delta T$  was calculated over equivalent hydration time t<sub>eq</sub>. The maximum (potential) heat enthalpy Q<sub>pot</sub> (J/g) was calculated after the method proposed by Rostasy and Krauß (2001), taking account of the specific cement ratio. Hence, Qpot decreases when OPC is replaced by inert additives. For simplification we assume that silica fume is inert, which is tolerable for small replacement rates and considering the low reacted part of silica fume at very early age. Consequently, the contribution to hydration heat development is ascribed only to the OPC, resulting in higher hydration degrees for OPC-S1 pastes. The potential heat rise  $\Delta T_{pot}$  was calculated using the following specific heat capacities of the components:  $c_c = 0.754 \text{ J/(g·K)}$  for cement,  $c_w = 4.187 \text{ J/(g·K)}$  for water,  $c_f = 1.0 \text{ J/(g·K)}$ for limestone and clay,  $c_f = 0.835 \text{ J/(g·K)}$  for quartz and  $c_f = 0.85 \text{ J/(g·K)}$  for silica fume. With the assumption of the specific heat capacities being constant over time, the approximation  $Q(t_{eq})/Q_{pot} = \Delta T(t_{eq})/\Delta T_{pot}$  is valid. The hydration degree is then calculated as  $\alpha(t_{eq}) = \Delta T/\Delta T_{pot}$ . For full hydration (w/c)eff must exceed the value of 0.443, as reasoned by Krauss and Budelmann (2010). Consequently, the maximum hydration degree is lower than 1 for some paste mixtures. Krauss and Budelmann (2010) demonstrated that hydration degrees from calorimetry are in good agreement with hydration degrees from chemical bound water estimated by the loss on ignition method.

#### 3 RESULTS AND DISCUSSIONS

In figure 2 examples of calculated hydration degree curves are shown. The curves are approximated with the empirical model of Jonasson et al (1995) constituting a sigmoid curve which is described by three parameters:  $t_1$  (offset),  $\kappa_1$  (inclination) and  $\lambda_1$  (fit parameter), see eq. (1). The fit parameter  $\lambda_1$  wasn't used here. The fit was performed from  $t_{eq} = 2$  hrs to 120 hrs with the method of least squares. Some fitted curves are displayed in figure 2. Obviously, the fit with the Jonasson model is not excellent at very early age, but it becomes better after 48 hrs.

$$\alpha(t_{eq}) = \exp\left[-\lambda_1 \left(\ln\left(1 + \frac{t_{eq}}{t_1}\right)\right)^{-\kappa_1}\right]$$
(1)

The approach of Kondo and Daimon (1969) was adopted to quantify the filler impact on hydration kinetics. For that, the 1<sup>st</sup> derivation of the  $\alpha(t_{eq})$  curves  $d\alpha/dt$  and the 2<sup>nd</sup> derivation  $d\alpha^2/dt$  were calculated. The principle is presented in figure 3. The begin of acceleration stage III (S<sub>III</sub>) is denoted t<sub>i</sub>, the time of maximum heat release (transition from hydration stage III to IV) is t<sub>1</sub>, the hydration degree at time t<sub>1</sub> is  $\alpha_1$ , and the maximum hydration rate at time t<sub>1</sub> is k<sub>1</sub>. The parameters k<sub>2</sub>, k<sub>3</sub> and k<sub>4</sub> characterize the acceleration and deceleration rates in stages III and IV. In table 2 results for pastes with replacement rates f = 0.05 are given.

The results demonstrate the different effects of the individual fillers on hydration kinetics. The end of the induction period  $t_i$  is nearly the same for all mixtures. Only the micro quartz Q2 (retardation) and the clay powder C1 (slight acceleration) change the onset of stage III. C1 and silica fume S1 cause the greatest acceleration in stage III in comparison to pure OPC ( $k_3$  is +40% resp. +44%), which is probably due to their high specific surfaces. For limestone powders  $k_3$  is greater than for quartz powders, but the effect seems to be influenced distinctly by the fineness. This indicates that the acceleration effect is caused by the additional nucleation sites for hydration products provided by the surfaces of the inert particles, but also by the mineralogical characteristics of the surfaces. Limestone particles seem to have a higher "affinity" to hydration products than quartz particles, though Q2 has a much greater BET surface than L1 and L2. We must expect that for limestone powders with similar fineness as C1 or Q2 k<sub>3</sub> would further increase. Unfortunately, limestone cannot be ground to specific surfaces  $> 15 \text{ m}^2/\text{g}$  (BET) due to the limited grindability (strong agglomerations). The values for k<sub>2</sub> show similar tendencies as k<sub>3</sub>. Obviously, for some of the powders the transition from stage III to stage IV takes place earlier for great values of  $k_2$  and  $k_3$ . This effect is distinct for S1 and C1 and rather small for L1 and L2. Quartzes even prolong stage III, which is unexpected for Q2.



Figure 2. Hydration degree and fits with the Jonasson equation



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	$\alpha_1$	t <sub>i</sub>	$t_1$	$k_1$	$k_2$	k <sub>3</sub>	$k_4$
·				$(\cdot 10^{\circ})$	$(\cdot 10^{\circ})$	$(\cdot 10^{\circ})$	$(\cdot 10^{\circ})$
OPC	0.116	2.1	8.6	29.9	8.72	4.72	1.57
5% S1	0.121	2.0	7.8	35.4	11.52	6.80	2.14
	+5%	-5%	-9%	+18%	+ <i>32%</i>	+44%	+36%
5% L1	0.126	2.0	8.6	33.3	9.96	5.32	1.87
	+8%	-6%	0%	+11%	+14%	+13%	+ <i>19%</i>
5% L2	0.126	2.2	8.3	35.1	10.84	5.72	2.05
	+8%	+4%	- <i>3%</i>	+17%	+24%	+21%	+31%
5% Q1	0.116	2.1	8.9	28.4	8.01	4.10	1.43
	+0%	+2%	+ <i>3</i> %	- <i>5%</i>	-8%	<i>-13%</i>	-9%
5% Q2	0.128	2.4	8.7	34.6	10.27	5.29	1.97
	+10%	+12%	+1%	+15%	+ <i>18%</i>	+12%	+25%
5% C1	0.120	1.9	7.7	34.5	11.38	6.65	2.07
	+ <i>3</i> %	- <i>11%</i>	-10%	+15%	+ <i>30</i> %	+40%	+32%

Table 2. Fit parameters

Figure 3. Classification of hydration stages and definition of the fit parameters

equivalent time  $t_{eq}$  (h)

The parameter  $k_4$  characterizes the slowdown of hydration in stage IV. Again, the deceleration is very significant for mixtures with high values for k<sub>2</sub> and k<sub>3</sub>. But here also Q2 seems to retard further hydration processes. Only Q1 enhances hydration in stage IV as compared with pure OPC. This is illustrated in figure 4 by the slopes of hydration rates  $d\alpha/dt$  in stages III and IV for C1 and Q1 in comparison to pure OPC. For C1 we have to notice that for higher replacement rates the acceleration in stage III is stronger, but also the negative slope in stage IV. For Q1 a higher replacement rate leads to better results in both hydration stages.

With regard to the results, the following reasons could be considered. The transition from hydration stage III to stage IV is most often attributed to a change in the rate limiting hydration processes. In stage III the nucleation and growth processes are rate limiting. The hydration rate is determined by the ion concentrations in the pore solution and the surfaces available for the precipitation of products. The nuclei grow on reactive and on inert particles surfaces into planar directions until the surfaces are totally covered with hydration products. Parallel also a growth into the orthogonal direction takes place in a smaller extent. After the cement particles are surrounded by a concentric hydration product layer the hydration rate is governed by diffusion of ions through this layer. When the product layer is thick or very dense at the transition time  $t_1$ , the hydration rate drops faster in stage IV because diffusion through this layer is slow. Hence, very fine fillers must have an influence on the product layer thickness or its density.

This effect could originate from the particles allocation in the fresh paste, e.g. on cement particles surfaces or in the free pore space. If the particles were situated mainly in the pore space a higher product volume should be produced before the cement particles surfaces are covered with hydration products. Hence, hydration degree  $\alpha_1$  at transition time t<sub>1</sub> must be higher. In table 2 we can see that  $\alpha_1$  increases only slightly for C1 and stage III is finished earlier than in case of pure OPC or limestone powders. An explanation could be, that a significant percentage of the clay particles is coagulated on the cement particles surfaces whereas limestone and quartz particles are located to a greater part in pore space. In case of clay particles the consequence would be that most of the nuclei are nearby the cement surface, thus leading to an earlier coverage of the cement surface with hydration products. This could explain the very high hydration rate in stage III, the early transition to stage IV and the steep drop of the rate curve in stage IV for the clay powder C1.



Figure 4. Examples of hydration rate curves

For limestone powders this hypothesis could explain the higher values for  $\alpha_1$  and  $t_1$ , as compared to clay and silica fume although the rates  $k_2$  and  $k_3$  are smaller. As stated above, tests with limestone of similar BET fineness are needed for final conclusions, which is not possible.

The reasons for the influence of mineralogical characteristics on coagulation and on hydration kinetics will be discussed in the following. For very small particles the interparticle forces are determining the coagulation behavior and the spatial distribution. In dense suspensions with high pH values particle distances are small and the double layer after the DLVO (Derjaguin – Landau – Verwey – Overbeek) theory is very thin, as argued by Budelmann et al (2007) and others. Then, the attractive van der Waals forces become predominant resulting in coagulations, which is especially true for very small particles with diameters < 1  $\mu$ m. The intensity of the coagulations is determined by the solid content, the particle size, the ion concentration, the ion species, the electric potential and the Hamaker constants of the minerals. After Geisenhanslüke (2009) the Hamaker constants are 1.7  $\cdot 10^{-20}$  J for SiO<sub>2</sub>, 4.2  $\cdot 10^{-20}$  J for Al<sub>2</sub>O<sub>3</sub>, and 2.2  $\cdot 10^{-20}$  J for CaCO<sub>3</sub>. Hence, particles with aluminatic surfaces, such as clay particles, coagulate much stronger than limestone particles.

Another reason is the different electric potential of the individual particles in high pH solutions. For quartz the isoelectric point (IEP) is at pH = 3.7 and for aluminates at pH = 9.1, see Geisenhanslüke (2009). Carty (1999) reported IEP values between 8.5 - 10.4 for aluminium hydroxides, e.g. a part of the kaolinite surfaces. For calcium carbonate no clear values were found. For pH values > 12 all three types of surfaces have different negative electric potentials (expressed by the zeta potential). While quartz surfaces are highly negative, aluminatic and carbonatic surfaces are charged only slightly negative, see Rahhal et al (2009). Zeta potentials smaller than |+/-10 mV| enforce particles coagulation because the repulsive electrostatic forces of equally charged surfaces become small compared to the van der Waals forces. After that theory quartz particles coagulate to a lesser extent than limestone and clay particles. As demonstrated by Budelmann and Krauss (2009) the paste viscosity corresponds to that theory: cement pastes with quartz powder showed the lowest yield values followed by limestone powder, whereas clay powder had the highest yield value. A good support for the hypothesis is given by SEM images. As Budelmann and Krauss (2009) showed in their presentation a great part of the clay particles were attached to the cement surfaces in fresh suspensions.

Due to their coagulation behavior quartz powders with very high specific surfaces provide a better "filler effect" than clay and limestone powders. This was approved by the good performance of Q2 regarding the strength and the chemical bound water, as presented by Budelmann and Krauss (2009). On the other hand, C1 can be used for the enhancement of rheology and short term hydration kinetics.

Rahhal et al (2009) explained the preferential growth of calcium hydroxide (CH) on limestone surfaces by the specific absorption of  $OH^-$  and  $Ca^{++}$  ions from the pore solution. Also CH directly coagulates on carbonate surfaces due to the low zeta potential. After that, quartz particles with highly negative zeta potential absorb CH from the pore solution to a much lesser extent. Further, they don't coagulate preferentially on cement surfaces with low zeta potential.

A further explanation could be the influence of fillers with different electric potential on the ion absorption processes of cement particles. As Yoshioka et al (2002) stated, the cement clinker phases  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  are charged differently and thus specifically absorb alkali, calcium and sulphate ions from the pore solution. Those absorption processes could be altered by the fillers, resulting in an alteration of chemical processes and in a modified CH formation. Those aspects will be discussed elsewhere in more detail.

## 4 CONCLUSIONS

It was demonstrated that the hydration rates and the forms of the kinetic curves depend on the fineness, the electrochemical and the mineralogical characteristics of the individual fillers. Explanations were given for the influence of mineralogy, specific surface and electric potential in high pH solutions on hydration rates of cement-filler systems at early ages. It becomes clear that analytical kinetic models based on the dilution effect only give satisfactory results when long term processes and macroscopic characteristics are of interest. In order to adequately predict kinetics and microstructure development of cement pastes with very fine fillers, models are requisite that enable the consideration of individual spatial distributions, solution and precipitation processes as well as diffusion processes. For that, deeper knowledge is needed on the alteration of chemical processes, hydration product formation and the spatial distribution of particles. Currently, further research is in progress to validate the hypotheses presented here and to develop kinetic models.

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