

EFFECT OF MATERIALS ON SEDIMENTATION OF CEMENT PASTE

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ABSTRACT

A conceptual model for the stability of paste was proposed and an experimental system, HYdroStatic Pressure Test (HYSPT), was developed for detecting the sedimentation of fresh cement paste. By accurate measurements of the hydrostatic pressure, p , at a depth h and time t , both sedimentation rate and state of flocculation are assessed from pressure drop vs. time curves (dp/dt). Material parameters like solid fraction, water reducer, VMA and limestone replacement were studied with HYSPT. For normal cement paste with high solid fraction (Φ), as Φ increases ($w/c = 0.7 - 0.4$), the sedimentation is speeded up. Dispersion of the particles by water reducers has a clear effect of slowing down the movement and producing less clear sedimentation plateau pressures. This effect is clearer for limestone slurries of varying Φ than for cement pastes, so cement needs more SP than limestone filler to be dispersed and behave according to the Richardson-Zaki equation. At 40 % limestone replacement (causing increase of w/c from 0.5 to 0.835 to keep Φ constant) 0.6 % SP stabilized slightly better when added as mass fraction of powder than when added as mass fraction of cement. Thus, limestone gave improved stability at higher total SP content and w/c . VMA enhanced stabilization only when combined with water reducer. Finally we propose that time of set can be defined at the onset of the plateau as particle movement stops.

1 INTRODUCTION AND BACKGROUND

Stability of fresh SCC and cement paste is complicated and governed by mechanisms acting on several scales involving viscous flowing / bleeding, movement of fine particles during the induction period of cement hydration and larger aggregate segregation. The instability of cement paste itself happens due to sinking of powder ($\leq 125\mu\text{m}$ according to the particle-matrix model [1]). This particle sinking process, also named sedimentation, is influenced by several factors: density differences, viscous flow of the liquid [2], dissolution, shrinkage and early hydration of the organic particles such as cement [3,4], thixotropy and structural buildup of the paste [5,6], dispersing / retarding / stabilizing effect by the admixtures [7]. All of the above factors are corresponding to the different influences of the materials on sedimentation.

In our previous work, some theories on concrete stability and particle sedimentation have been reviewed [8] and a conceptual model for the stability of cement paste was proposed [8,9]. Based on Kynch theory [10] and Richardson-Zakis equation [11] sedimentation is dominated by the solid volume fraction Φ of the suspension. Fitch corrected the Kynch theory by explaining how the suspension-sediment interface rises with time for compression zones [12]. The Fitch paragenesis diagram was proposed in which the sedimentation types of the suspension are defined according to the solid concentration and flocculent state [13]. However, as already mentioned, the sedimentation process of cement paste is more intricate. Some investigations have focused on the sedimentation of cement paste. Mikanovic and Jolicoeur [14] discussed the influence of superplasticizers on the rheology and stability of limestone and cement pastes based on electrical conductivity and admixture adsorption measurements. Neubauer [7] studied inter-particle potential and the effect of admixtures on sedimentation behavior of cement suspensions based on DLVO theory from a microstructural aspect. However, these analysis methods for measuring the sedimentation are hard to apply for real cement paste with high solid fraction and complicated powder composition. Perrot et al. [15] discussed instability of the cement paste from the correlation between yield stress and bleeding instead of sedimentation. However, according to our investigation [9], the inhomogeneous parts of the cement paste below the bleeding water are also worthy to be studied since they affect the long-term properties of the paste and concrete. More recently the compressing properties of fresh cement paste were also investigated by Colombo et al. [16] with numerical simulations. There thus seems to be ongoing research due to lack of understanding about the whole

sedimentation process, the testing method to evaluate this process of cement paste and how materials influence this process. In previous research, a 4-stages conceptual model for the sedimentation and bleeding of the cement paste has been proposed, as Fig. 1 shows. Accordingly, an experimental system, HydroStatic Pressure Test (HYSPT), was developed for detection of the sedimentation of cement paste during its fresh state.

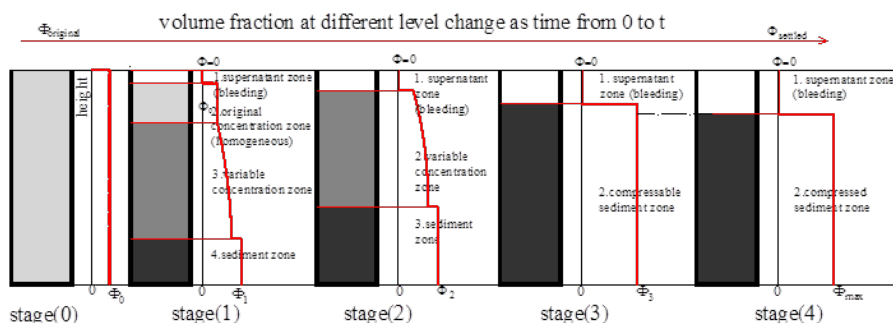


Fig. 1 - Conceptual model for sedimentation and bleeding

The application of HYSPT relies on that the mainly restricted Stokesian settlement of particles causes changes in solid fraction, Φ , and thus changes the fresh density, ρ , at a given height, h , and time, t . In a homogeneously settling zone the hydrostatic pressure, p , reduces according to $p(t,h) = \rho gh = [(\rho_l (1-\Phi(t,h)) + \rho_s \Phi(t,h))]gh$. Here ρ_l is liquid density and ρ_s is solid particle density [17]. By accurately measuring p at depth h and time t , both solid fraction and state of flocculation can be assessed from pressure drop vs. time curves (dp/dt). Assuming homogeneous zone, see Fig.1, we have $\rho = p/gh$ which can be written $m/V = p/gh$ and thus $m/Ah = p/gh$ so that $m/A = p/g$ with $A =$ Area of sedimenting particle flow. Therefore the initial sedimenting particle flow in homogeneous zone, J ($kg/m^2 \cdot s$) = d/dt (m/A) = d/dt (p/g) = $1/g$ (dp/dt). In our previous research, the applicability and repeatability of HYSPT for fresh cement paste has been described [9]. Factors like chemical shrinkage, orientation of pressure detection, dissolved salt etc. were found to be negligible during the induction period compared to the effect of sedimentation and flocculation for cement paste with normal $w/c=0.5$, and bleeding could be predicted [9]. Here we study the effect of composition and varying additions on the sedimentation process of fresh cement paste.

2 EXPERIMENTS AND MATERIALS

HYSPT was used to detect the sedimentation process of a series of suspensions. Fig. 2 shows the HYSPT setup with two positions for $p(t,h)$ at the depths $h_b=200\text{mm}$ and $h_m=110\text{mm}$. The pressure sensors are capable of detecting hydrostatic pressure with an accuracy of 0.75Pa . The test is done by mixing paste, pouring it into the cylinder and covering it with a lid to prevent evaporation.

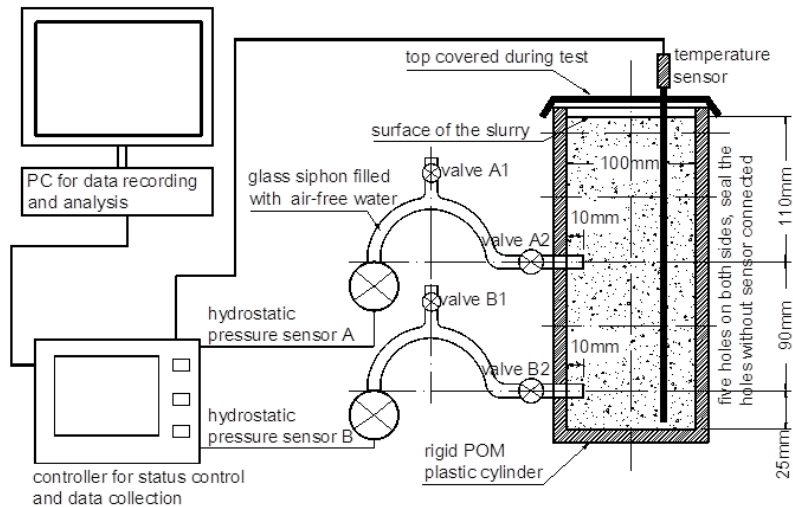


Figure 2 - HYSPT setup for sedimentation measurement [9]

As explained before, during the fresh state of cement paste, the total hydrostatic pressure drop and the final pressure plateau seem to be mainly controlled by particle sedimentation. The influence of pressure detection orientation (i.e. stress redirection), chemical shrinkage and static yield stress buildup of the cement paste does not overshadow this effect within the fresh period of the cement paste [9]. However, as structural build-up progresses/after set, the suction increases rapidly [3,4]. So defining the fresh state is important for hydrostatic pressure analysis. By Vicat test, the initial setting time of the cements used here is around 120 min. However, this period is highly affected by the addition of additives such as superplasticizer. Therefore heat evolution measurements (conduction calorimeter) were done for some cement pastes to determine the induction period. In our case, the fresh state of cement paste is defined as the phase before the initial hydration begins. The suspension volumes used for HYSPT are 2L and the mixing procedure was given in [9]. Due to the

small amount of sample (about 6g) required for calorimeter tests, around 100ml cement pastes were mixed by a 600Watt hand mixer at middle rotation speed with the same mixing sequence as that for HYSPT.

The chemical composition and physical characteristics of cement (standard fly ash cement STD-FA CEM II, Portland cement STD-CEM II) and limestone filler are given in Table 1. Two types of (super)plasticizers, pc for polycarboxylate and ls for lignosulfonate, are used in the experiments, as shown in table 2 with the main characteristics. The proportions of the tested suspensions are shown in table 3-4.

Table 1: Chemical composition (wt. %) and physical characteristics of the two types of cements and limestone filler.

	CEM-FA	Portland cement	Limestone
SiO ₂	25.04%	20.98%	16.03%
Al ₂ O ₃	7.87%	5.13%	3.29%
Fe ₂ O ₃	4.37%	5.13%	2.39%
CaO	52.50%	60.61%	76.40%
MgO	1.78%	2.39%	2.09%
P ₂ O ₅	0.26%	0.14%-	
K ₂ O	0.97%	0.86%	0.76%
Na ₂ O	0.80%	0.43%	0.34%
SO ₃	-	3.01%	0.50%
Blaine [m ² /kg]	452	382	361
D ₅₀ [μm]	12.9	13.3	17.9
Specific weight [g/cm ³]	2.98	3.15	2.78

Table 2 - Main characteristics of the (super)plasticizers

	PC	LS
Viscosity* (mPa·s)	Low, <30	Low, <30
Solid content	30.0±1.5	39.0±2.0
Specific gravity (g/cm ³)	1.09±0.02	1.20±0.03
pH-value	6.5±1	8.0±1
Chloride content (%)	<0.01	≤0.1
Alkali (Na ₂ O equivalent) (%)	<2.5	≤6

*Viscosity is measured by Brookfield Viscometer, DV-1, LV1, 100rpm, 20±2°C

The particle size distributions of the cements and limestone filler determined by laser diffraction are shown in Fig. 3. The two types of cement particles have similar size distribution and are a bit finer than the limestone filler, also seen from Blaine and D₅₀ in table 1.

Table 3 - The recipes of all the tested suspensions in Fig. 4 - Fig. 8

Test No.	Test	Figure No.	Code in the figure	cement type	w/c	w/b	w/p	solid fraction Φ	(super)plasticizer (SP) type	SP dosage	filler replacement	VMA dosage
1			$\Phi 0.459$		0	0	0.436	0.459	no	0	100% limestone	0
2	HYSPT	Fig. 4	$\Phi 0.404$		0	0	0.546	0.404	no	0	100% limestone	0
3			$\Phi 0.361$		0	0	0.655	0.361	no	0	100% limestone	0
4			$\Phi 0.326$		0	0	0.765	0.326	no	0	100% limestone	0
5			$\Phi 0.459$ -pc0.3		0	0	0.436	0.459	polycarboxylate	0.3% lbwc	100% limestone	0
6			$\Phi 0.404$ -pc0.3		0	0	0.546	0.404	polycarboxylate	0.3% lbwc	100% limestone	0
7	HYSPT	Fig. 5	$\Phi 0.361$ -pc0.3		0	0	0.655	0.361	polycarboxylate	0.3% lbwc	100% limestone	0
8			$\Phi 0.326$ -pc0.3		0	0	0.765	0.326	polycarboxylate	0.3% lbwc	100% limestone	0
9			$\Phi 0.459$ CEM-FA		0.5	0.4	0.4	0.459	no	0	0	0
10	Calorimetry		$\Phi 0.404$ CEM-FA		0.625	0.5	0.5	0.404	no	0	0	0
11	test	Fig. 6	$\Phi 0.361$ CEM-FA		0.75	0.6	0.6	0.361	no	0	0	0
12			$\Phi 0.326$ CEM-FA		0.875	0.7	0.7	0.326	no	0	0	0
13			$\Phi 0.459$ CEM-FA		0.5	0.4	0.4	0.459	no	0	0	0
14			$\Phi 0.404$ CEM-FA		0.625	0.5	0.5	0.404	no	0	0	0
15	HYSPT	Fig. 7	$\Phi 0.361$ CEM-FA		0.75	0.6	0.6	0.361	no	0	0	0
16			$\Phi 0.326$ CEM-FA		0.875	0.7	0.7	0.326	no	0	0	0
17	Calorimetry		$\Phi 0.404$ -pc0		0.625	0.5	0.5	0.404	polycarboxylate	0	0	0
18	test	Fig. 8	$\Phi 0.404$ -pc0.3		0.625	0.5	0.5	0.404	polycarboxylate	0.3% lbwc	0	0
19			$\Phi 0.404$ -pc1.2		0.625	0.5	0.5	0.404	polycarboxylate	1.2% lbwc	0	0

Note: 1. "lbwc" means liquid by the weight of the cement; "lbwb" means liquid by weight of powder;

2. the solid fraction is calculated assuming no air voids in the cement pastes.

Table 3 (continued) - The recipes of all the tested suspensions in Fig. 9, Fig. 11-12 and Fig. 14

Test No.	Figure No.	Code in the figure	cement type	w/c	w/b	w/p	solid fraction Φ	(super)plasticizer type	(super)plasticizer dosage	vol. based filler replacement	VMA dosage
20		$\Phi 0.459$ -pc0.3	CEM-FA	0.5	0.4	0.4	0.459	polycarboxylate	0.3% lbwc	0	0
21	HYSPT	$\Phi 0.404$ -pc0.3	CEM-FA	0.625	0.5	0.5	0.404	polycarboxylate	0.3% lbwc	0	0
22		$\Phi 0.361$ -pc0.3	CEM-FA	0.75	0.6	0.6	0.361	polycarboxylate	0.3% lbwc	0	0
23		$\Phi 0.326$ -pc0.3	CEM-FA	0.875	0.7	0.7	0.326	polycarboxylate	0.3% lbwc	0	0
24		pc0	CEM-FA	0.625	0.5	0.5	0.404	polycarboxylate	0	0	0
25	HYSPT	pc0.3	CEM-FA	0.625	0.5	0.5	0.404	polycarboxylate	0.3% lbwc	0	0
26		pc0.6	CEM-FA	0.625	0.5	0.5	0.404	polycarboxylate	0.6% lbwc	0	0
27		pc1.2	CEM-FA	0.625	0.5	0.5	0.404	polycarboxylate	1.2% lbwc	0	0
28		pc0-lim0	Portland	0.5	0.5	0.5	0.388		0	0	0
29	HYSPT	pc0.6C-lim0	Portland	0.5	0.5	0.5	0.388	polycarboxylate	0.6% lbwc	0	0
30		pc0.6C-lim0.4	Portland	0.835	0.84	0.526	0.388	polycarboxylate	0.6% lbwc	40% limestone	0
31		pc0.6P-lim0.4	Portland	0.835	0.84	0.526	0.388	polycarboxylate	0.6% lbwp	40% limestone	0
32		pc0VMA0	Portland	0.5	0.5	0.5	0.388		0	0	0
33		pc0VMA1.0	Portland	0.5	0.5	0.5	0.388		0	0	1.0
34		pc0VMA2.0	Portland	0.5	0.5	0.5	0.388		0	0	2.0
35	HYSPT	pc0.6VMA0	Portland	0.5	0.5	0.5	0.388	polycarboxylate	0.6% lbwc	0	0.0
36		pc0.6VMA1.0	Portland	0.5	0.5	0.5	0.388	polycarboxylate	0.6% lbwc	0	1.0
37		pc0.6VMA2.0	Portland	0.5	0.5	0.5	0.388	polycarboxylate	0.6% lbwc	0	2.0

Note:

1. "lbwc" means liquid by the weight of the cement; "lbwb" means liquid by weight of powder;
2. the solid fraction is calculated assuming no air voids in the cement pastes.

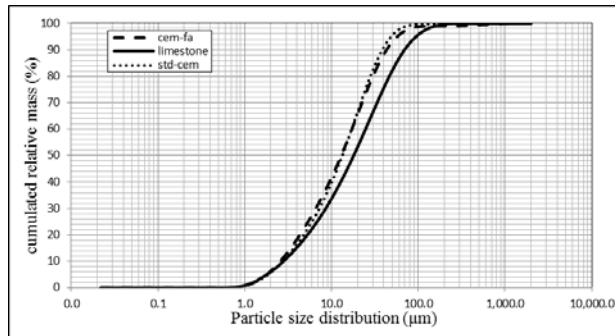


Fig. 3 - The particle distribution of the cement and limestone powder

The recipes of all the tested suspensions are shown in table 3 with the same order as shown in the relative figures:

3 RESULTS AND DISCUSSION

3.1 Solid volume fraction without/with super plasticizer

Figures 4 – 14 give the results, mainly as time vs hydrostatic pressure. The Richardson-Zaki equation [11], which will frequently be cited, is written as $u_s = u_{\infty}(1-\Phi)^n$, in which u_{∞} is the Stokes terminal velocity, u_s is the multiple particles' sinking velocity and n is a coefficient depending on the size ratio between container and particle (normally $n=4.65$). The equation predicts that the higher the solid volume fraction of the suspension is, the more the sinking velocity of the particles is reduced compared to Stokes terminal velocity. To validate this effect, HYSPT was first used to monitor the sedimentation process of the suspensions with inert limestone. These experiments show the pressure drop due to the particle sedimentation without any influence from particle hydration or, say, structural buildup of the suspension. As shown in table 3, the solid fractions of the limestone slurries are the same as the corresponding cement pastes with w/c from 0.4 to 0.7. Fig. 4 shows the pressure change with time at two different heights; left plot for bottom (20cm below the surface of the suspension, see Fig. 1) and right plot for middle (11cm below). All HYSPT results are shown in this way in Figures 4 - 14.

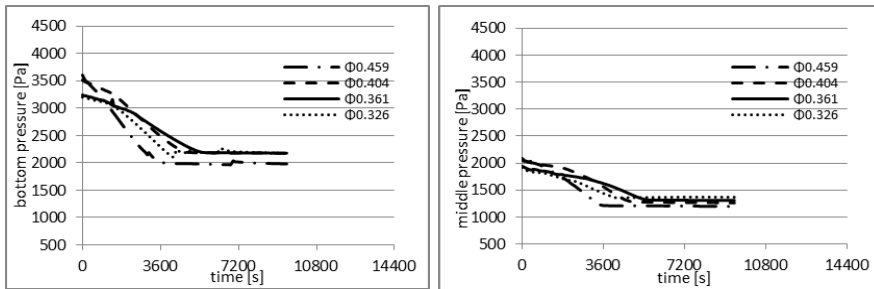


Fig. 4 - Hydrostatic pressure vs time curves by HYSPT for the limestone slurries with different solid volume fractions, no superplasticizer (SP)

It can be seen that as the particles were sinking, the pressure detected at some level dropped gradually and finally reaches a plateau when the sedimentation process finishes and all particles settled at the bottom of the container or were supported by particles below. The time to reach the plateau is the settling time at this height and varies for different suspensions. According to the order of the pressure drop curves, it seems that the Richardson-Zaki equation does not hold for the slurries with this range of solid fraction since dp/dt , and thus sinking speed in the homogeneous zone in figure 1, increases with increasing Φ , see figure 4. This is contrary to the R-Z prediction and mainly because of the different particle flocculation states for suspensions with different Φ . The agglomerated or flocculated particles have bigger “particle” size causing higher sinking velocity according to Stokes law [18]. (The HYSPT results of paste with SP showed that the Richardson-Zaki equation holds better for the suspensions without flocculation, see next session.) After the sedimentation process finishes, the pressure at the plateau is close to the hydrostatic water pressure. Differences in plateau pressures are due to differing slurry densities due to varying amounts of very fine particles sinking at almost zero speed above the measuring point and small deviations in filling height in the cylinder.

Fig. 5 shows dp/dt of equal slurries made with 0.3% lbwp (liquid by weight of powder) dosage of polycarboxylate superplasticizer (pc SP). It can be seen that SP helps to disperse the particles and effectively reduces the flocculation state of the cement particles. Thus the average sinking velocity of the particles is reduced. This can be seen as longer time of pressure drop. It can be seen that in the first hour for both pressure curves (middle and bottom), the slurry with higher solid fraction had lower pressure drop gradient and thus a lower particle sinking velocity. This coincides well with the Richardson-Zaki equation contrary to the mixes

without SP shown in Fig.4. So it seems that the particle flocculation is an important reason for instability of suspensions with high solid fraction. Based on Fig.4 and Fig.5 it seems that the Richardson-Zaki equation, which should be written on the form $u(h,t)_s = u_\infty(1-\Phi(h,t))^n$, is too simple to take into account both the phenomenon of flocculation and increased solid fraction towards the bottom as the particles sink unless the state of flocculation is known. It also can be seen that the sedimentation process has been prolonged by the dispersing effect of SP.

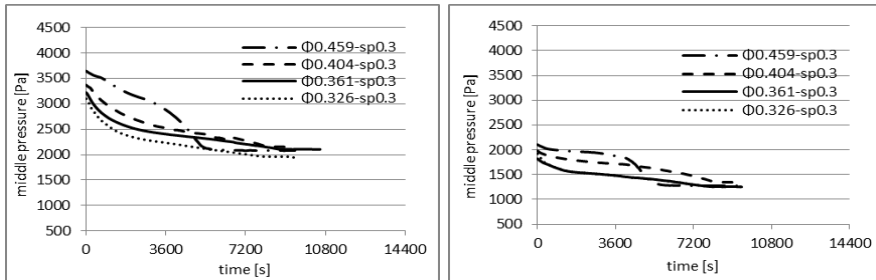


Fig. 5 - Hydrostatic pressure vs time curves by HYSPT for limestone slurries with varying solid fractions and 0.3 % SP

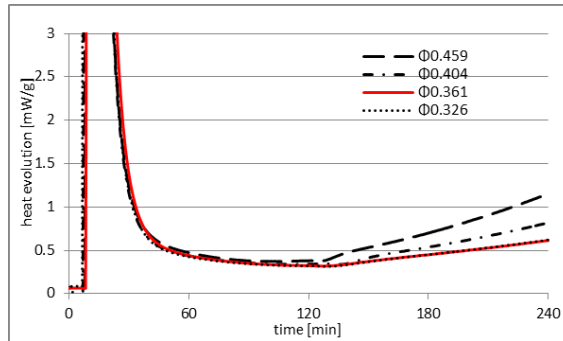


Fig. 6 - the heat evolution curves of cement pastes with different volume fraction and without SP

Fig. 6 shows calorimeter tests carried out to check the induction period (within 4 hours) for $w/c = 0.4 - 0.7$ without SP before comparing the pressure drop curves of cement pastes with different volume fractions. It can be seen that all the cement pastes have induction periods of around 2 hours. In this period, the pressure drop of the cement paste is mainly controlled by the particle sinking (pure sedimentation) with very limited influence by the paste early structural buildup and chemical shrinkage, as

investigated in [9]. Powerful suction with negative pressures developed for all pastes later as measured until app. 8 hours.

Fig. 7 shows the pressure results for the fly ash cement pastes with different solid fractions having $w/c=0.4$ to 0.7 .

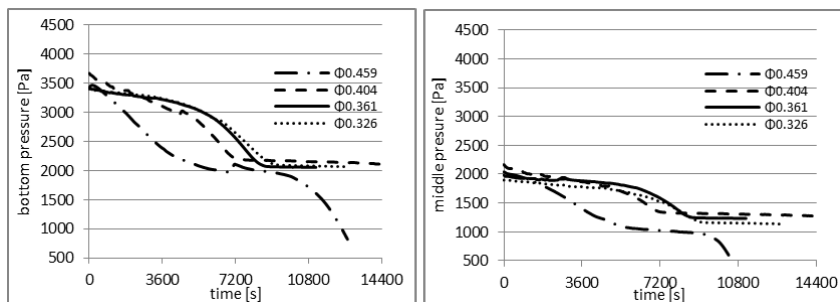


Fig. 7 - Hydrostatic pressure vs time curve by HYSPT for the fly ash cement pastes with different solid volume fractions and without SP

The time to reach the plateau of the cement pastes is clearly later than that of the limestone slurries. This is reasonable due to its finer particle sizes and thus slower sedimentation. The coarser limestone particles give faster sinking velocity and accordingly the limestone slurries reach the plateau faster. However, dp/dt of the cement pastes with different Φ show similar orders as those of the limestone slurries. However, the inflection points of the pressure drop curves of pastes are less clear than those of limestone slurries. This could be related to finer particles, possibly early dissolution and the structural buildup of the pastes. However, by comparing the sedimentation of the suspensions with these two powders, it seems that during the fresh state of cement paste, the total hydrostatic pressure drop and the final pressure plateau seem to be mainly controlled by particle sedimentation. The influence by chemical shrinkage and static yield stress buildup does not overshadow this effect, which is also investigated in detail in [9]. This statement is also based on in situ measurements of solid fraction with pipette and microwave oven during the first 2 hours [9]. The plateau pressures of cement pastes of $w/c=0.5\sim 0.7$ are similar to those of limestone slurries, indicating the applicability of HYPST for stability detection. For cement paste with $\Phi=0.459$ the plateau pressure reached before 2h is close to that of water, indicating support from the bottom. Then pressure shows a sharp drop a bit more than one hour after reaching the plateau, which indicates the effect of strong hydration of cement. This is app. $2\frac{3}{4}$ h after mixing so this period is the limit of applicability of HYSPT for this cement paste.

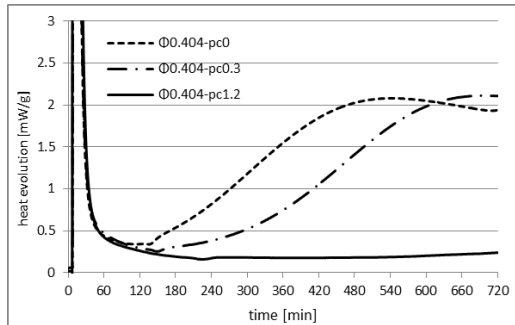


Fig. 8 - the heat evolution curves by calorimetry for the fly ash cement paste ($\Phi=0.404$) with different dosages of pc SP

From Fig. 8, it is clear that the induction period of the cement hydration was significantly prolonged with addition of SP. At higher dosage up to 1.2% lbwc, the induction period can reach up to 12 hours. Due to adsorption, de-flocculation and increased spacing of the particles, SP significantly delays the early set. Thus the induction period is prolonged and the fresh period of the cement paste with SP can be longer than 2 hours: around 3 hours for the paste with 0.3% of pc SP. HYSPT therefore is way of defining the time of set directly related to particle movement: at the onset of the plateau set starts. HYSPT can therefore be used as a new way of defining setting time, more related to particle sedimentation movement than to hydration.

Fig. 9 shows pressure drop curves for the cement pastes with 0.3% lbwc of pc SP. Comparing with Fig. 7, it is seen that even as low dosage as 0.3% lbwc prolongs the sedimentation processes of all cement pastes. The inflection points as the plateaus are reached seem more obscure, probably because some small micro- or nanoparticles sink at very low velocity. A soft layer of dilute grout, clearly different from the pastes without SP, can be seen between the supernatant (bleeding water) and sediment body, see Fig. 10 for the paste with 1.2% lbwc pc SP after sedimentation. Comparing Fig. 5 and 9, the SP effect for cement paste at this dosage seems less pronounced than for the limestone slurries. The order of the pressure gradients, dp/dt , for cement pastes with different solid fractions still indicate fastest movement at highest Φ . This indicates that the Richardson-Zaki equation does not hold for this series of proportions. This means that there are still different states of flocculation and thus 0.3% is not enough for cement paste with high solid fraction.

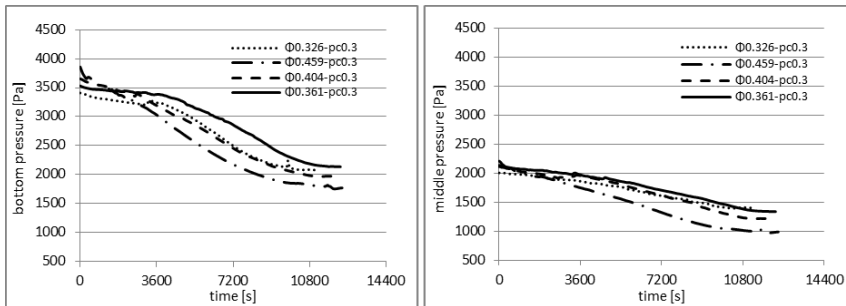


Fig. 9 - Hydrostatic pressure vs time curve by HYSPT for the fly ash cement pastes with different solid volume fractions and 0.3% pc SP

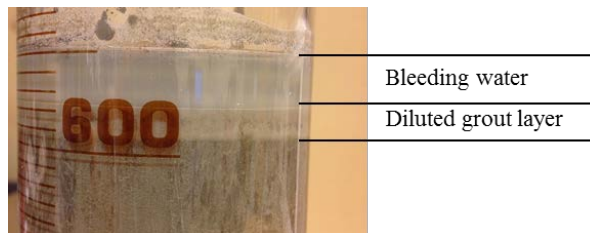


Fig. 10 – bleeding and diluted cement grout layers after sedimentation

Comparing Fig. 7 and Fig. 9 shows that the sharp drop of the pressure for paste $\Phi=0.459$ in Fig. 7 did not occur for paste $\Phi=0.459$ pc0.3 in Fig. 9. It indicates the strong effect of SP on cement hydration. Young [19] considered this to be an effect of nucleation. The organic compounds adsorb on the calcium hydroxide nuclei and hinder their future growth. Polycarboxylate SP influences the morphology and number of calcium hydroxide crystals formed in C_3S pastes, thus the crystallization (acceleration) period is delayed. Scherer [20] simulated this nucleation and growth process recently. Jennings [21] defined this nucleation and growth period in early age (middle period) to be 4~24h, which coincides with our case. However, in our point of view this middle period depends on the proportions and additives for the cement paste.

3.2 Effect of dosage of super plasticizer

SP contributes to the stability of cement paste by three effects: first and most important is the dispersing effect, which reduces the flocculation state and thus the real size of the sinking “particles” [22]. The second is to delay the early hydration because of adsorption on the surface of cement and influence on the nucleation as shown in Fig.8 [23]. The third is the

effect on the compatibility of cement-superplasticizer system [24]. All these three effects might influence the whole sedimentation process of the fresh cement paste. Fig. 11 presents this influence from different dosages of pc SP on the sedimentation process for $w/c = 0.50$.

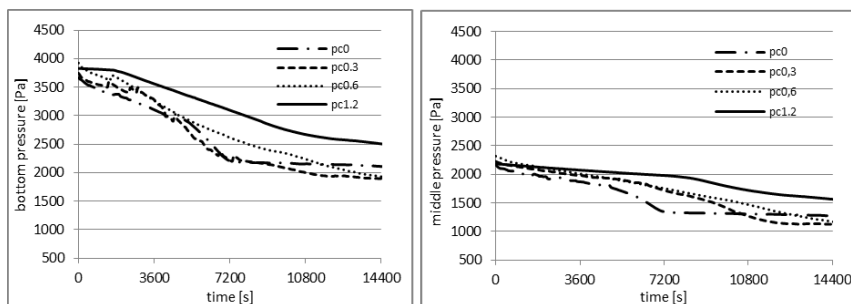


Fig. 11 - Hydrostatic pressure vs time curve by HYSPT for the fly ash cement pastes ($\Phi=0.404$) with different dosages of pc SP

Fig. 11 shows that the sedimentation process can be prolonged by adding higher dosage of SP. At the same time the dispersion by SP reduces sinking speed compared to without SP since flocculation causes larger effective particles and faster sinking. The net effect of stability thus is not quite clear. In the case of high dosage of SP (1.2% lbwc), the inflection point for the plateau is ambiguous, possibly a result of both particle sinking and the compression of the sediment zone, as suggested in Fig.1. In addition, the early dissolution / hydration and some bleeding water reabsorption also induce pressure drop; in the order of max 100Pa [9] before set.

3.3 Filler effect

SP contributes to stability of cement paste mainly as a result of the dispersing effect as discussed above. However, filler affects stability of fresh cement paste in a different manner. Ferraris et al. [25] studied the influence of mineral admixtures on the rheology properties of cement paste and concrete. Bonavetti et al. [26] and more recently Lothenbach et al. [27] investigated the effect of limestone filler on the early hydration of cement. According to Stokes Law [18] as modified for yield stress fluid by Roussel [28], the yield stress and viscosity of the fluid phase are two important factors for particle sedimentation. The influence of filler and its combined effect with SP on sedimentation were therefore also studied by

HYSPT. Fig. 12 shows the pressure drop curve of four pastes with limestone replacement and/or different dosages of pc SP.

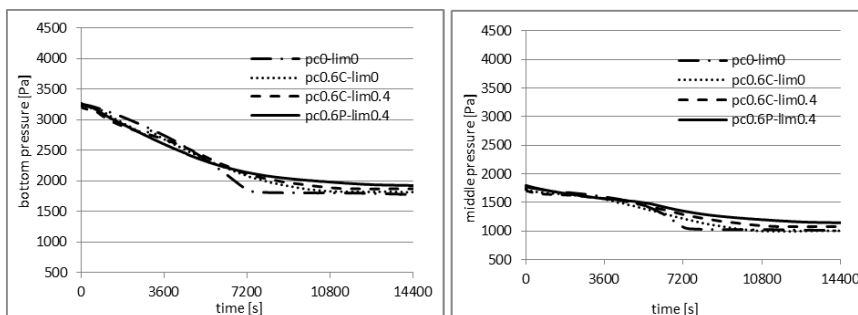


Fig. 12 – Hydrostatic pressure vs time curves by HYSPT for cement pastes ($\Phi=0.388$) with limestone replacement and different SP dosages

As presented in section 1, solid volume fraction is a governing factor in sedimentation, so all filler replacement in our study is volume based. The paste without limestone replacement and SP (pc0-lim0) is used as reference. Comparing the curves in Fig.12 for pc0.6C-lim0 and pc0.6C-lim0.4, it seems that 40% limestone replacement by cement volume did not affect the particle sedimentation process clearly. However, in these two cases pc SP dosage is 0.6% by cement mass, so for the sample pc0.6C-lim0.4 with 40% limestone replacement, the total amount of SP is less than that of pc0.6C-lim0 without filler. Thus, a filler effect by limestone powder therefore gives similar or even better stability properties than the paste without filler but less SP. To compare such a possible filler effect for cement pastes with the same SP dosage, HYSPT measurement was also carried out for the cement paste with the same volume based replacement of limestone, but with 0.6% pc SP by the total powder mass (here the liquid dosage is still a little bit lower though not that much, than the sample pc0.6C-lim0 due to the lower density of limestone filler). There is slightly more stabilizing effect when using the SP based on powder mass, seen as a slightly higher plateau. The differences between pc0.6C-lim0, pc0.6C-lim0.4 and pc0.6P-lim0.4 thus show that limestone may give a bit more stabilization effect for cement paste with enough SP.

3.4 Combined effect of super plasticizer and VMA

In addition to filler, Viscosity Modifying Agent (VMA) is used as stabilizer to increase the viscosity and cohesion of cement-based materials

[29]. VMA, also known as anti-washout agent, was categorized into 5 classes [30] among which the water-soluble polymer type is the most popular used. The VMA used in this study is one type of water-soluble biopolymer. Saric-Coric et al. [31] studied the combined effect of SP and this type of VMA. It was concluded that pastes with VMA exhibited significantly lower forced bleeding than without VMA, and also the effect of combined addition of SP and VMA lead to an increase of SP demand and longer setting time. However, there is a lack of understanding of the effect of VMA on the whole sedimentation process. Therefore some HYSPT measurements on the effect of VMA were made.

As its name implies, VMA should influence the viscosity of the liquid between the particles. The viscosity of the pure VMA used for the experiments is around 0.05Pa·s, around 50 times higher than pure water. When diluted with water, the viscosity is expected to reduce. Thus, firstly the viscosity change due to VMA addition was measured with parallel (serrated) plate configuration in a Physica rheometer with 1 mm gap. The measurement was done with $d\gamma/dt = 50 \text{ s}^{-1}$ in 10 measurement points with duration 6s between each, then at increasing $d\gamma/dt = 0.1\text{—}1000 \text{ s}^{-1}$ and finally at descending $d\gamma/dt = 1000 - 0.1 \text{ s}^{-1}$. Fig. 13 shows the viscosity, μ (Pa·s), of water and of VMA:water mixed with mass ratio 1:10 from flow curves as $\mu = \tau/(d\gamma/dt)$ with $\tau =$ measured shear stress (Pa). The VMA mix has 2-3 times the viscosity of the water so there is an effect on liquid viscosity by VMA. Since the VMA in the liquid in fresh concrete is probably more diluted the effect on Stoke velocity and on bleeding rate according to Kozeny-Carmans Equation (KCE) should be quite limited. In addition parts of the VMA might be adsorbed by powders. Thus there is a large potential for research on this including to understand VMA effects on the viscosity of real fluid from different pastes, how it affects Stokesian movement, KCE-type flow and observed stability.

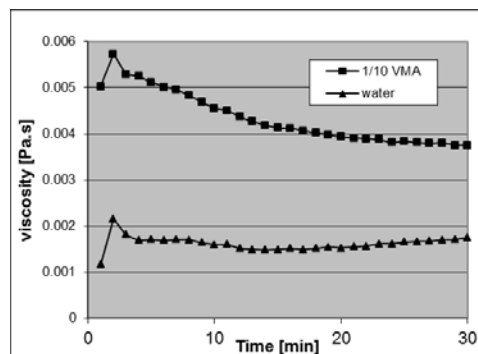


Fig. 13 – viscosity comparison water and diluted VMA/water of 1/10

Fig. 14 presents our initial studies of VMA using HYSPT showing curves for pastes with different dosages of VMA alone or combined with SP. The suggested dosage of this type of VMA is between 1 and 2 l per 100kg powder (1.0 and 2.0 in Fig. 14).

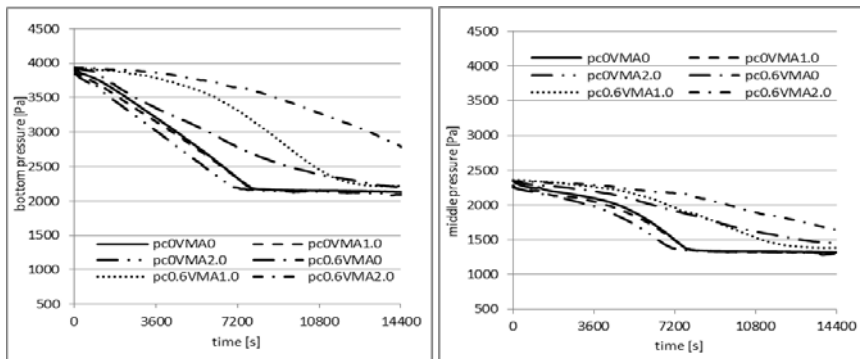


Fig. 14 - HYSPT-plots for cement pastes ($\Phi=0.388$) with VMA and with/without pc SP

For the case of adding VMA without SP, it is interesting to see that the sedimentation rate (which relates to dp/dt) of the paste with only VMA (pc0VMA1.0 and pc0VMA2.0) is unchanged or even slightly higher than that without admixtures (pc0VMA0). It means VMA possibly slightly accelerates the particle settling without SP although it increases the viscosity of the fluid. The reason for this is not known but could be due to more flocculation in the paste with high dosage of VMA. However, for the pastes with different dosages of VMA and the same SP (pc0.6VMA1.0 and pc0.6VMA2.0), the sedimentation process is distinctly prolonged so VMA is apparently activated in some way by the SP. The VMA addition has clearer effect on the sedimentation rate than just with SP (pc0.6VMA0). The higher VMA dosage further slows down the sedimentation process. The activation of VMA by SP is probably related to dispersion, making the smaller dispersed particles more sensitive to VMA effects than the larger flocculated agglomerates.

4 CONCLUSION

HYSPT reflects the sedimentation process for cement paste during fresh state via sensitive hydrostatic pressure measurements over time. The effect of solid volume fraction on sedimentation depends on the

flocculation state of the particles. Richardson-Zaki's equation is too simplified to take into account both the phenomenon of flocculation and sedimentation. This is seen from dp/dt on hydrostatic pressure vs time plots of pastes with different Φ . There dp/dt can change their order due to flocculation/dispersion depending on type of powder and use of SP. Limestone can stabilize paste as replacement for the cement; more so with the addition of superplasticizer. At 40 % limestone replacement and constant solid volume fraction (causing increase of w/c from 0.5 to 0.835), 0.6 % dosage of pc SP stabilized slightly better when being added by powder mass than by cement mass. VMA increases the viscosity of the fluid and can be an effective stabilizer when activated by superplasticizer. We propose that time of set can be described as the onset of the plateau of the HYSPT curves as particle movement stops.

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