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Rheological behavior as influenced by plasticizers and hydration kinetics

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Abstract

In the calcium aluminates cement – Portland cement – calcium sulfate based self leveling underlayments, the influence of raw materials on the properties such as rheology and hydration kinetics was considered. It was confirmed that calcium aluminates cement system formulation is suitable in cases where a short open time is required, and Portland cement system formulation is suitable in cases where a long open time is required with the result of flowability or rheology. And, in order to thin the viscosity of slurry, it turned out that the application of MF 2651F as a plasticizer and tartaric acid as a retarder were effective. Moreover, MF 2651F seldom delayed the hydration reaction compared with other plasticizers. The flow value and the yield stress showed correlation, without being dependent on the difference in formulation or a water powder ratio. This was considered to be because for the yield stress to relate to the fragility of the aggregation structure of slurry.

Keywords: Calorimetry; Rheology; Admixture; Calcium Aluminate Cement; Mortar

1. Introduction

Self-leveling underlayments (SLU) are principally used to produce a smooth and level floor surface on sub floors which are uneven, rough or unfinished concrete, cement mortar, plywood or ceramic tile floors etc. before the installation of carpets, ceramic tile, linoleum, vinyl tile, marble or wood. An SLU is required to make smooth a surface by itself and to harden rapidly without shrinkage and then to allow foot traffic in the shortest time possible after it is placed. In formulated SLUs hydraulically active minerals such as cements, limes and calcium sulphates (C$) are mixed with fillers, resins and admixtures [1]. Most of SLUs are either Portland cement (OPC) or C$ based. OPC based SLUs exceed C$ based SLUs in water resistant, high strength development, and short curing period. C$ based SLUs exceed OPC based SLUs in fast setting, permitting foot traffic sooner, less likely to crack and permitting without joint in a continuous placing [2].

In the meantime, the use of calcium aluminate cement in order to improve OPC based SLUs in specific properties such as rapid set, early strength, rapid drying and shrinkage compensation has been known. Such SLUs are usually consisted of three hydraulically active materials which are calcium aluminate cement (CAC), OPC and C$. The C$ may be used the form of gypsum, anhydrite or hemi hydrate plaster. Typical combinations are described in their locations on a ternary diagram CAC–OPC–C$ [1,3]. These combinations are either based on mixtures of CAC and C$ with eventually an addition of a lime source such as OPC or calcium hydroxide (CH) or on mixtures of OPC and CAC with eventually an addition of C$. The major hydrates formed in these combinations are given in Table 1 [1].

The purpose of this study is to investigate the influence of raw materials especially admixtures on properties such as workability, rheology and hydration kinetics in SLUs based on two binders. Additionally the influence of ageing on the properties such as rheology and hydration kinetics in SLU was examined.

2. Experiment

2.1. Formulations of SLU

Formulations of SLUs used in this study are based on two typical combinations which are shown in Table 2.

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Table 1
Major hydrates formed in CAC–OPC–C$

CAC+C$+OPC or CH, Ettringite system
$C_3A+3CaSO_4+32H_2O \Rightarrow C_3A{\cdot}3CaSO_4{\cdot}32H$
$3CA+3C\$+35H_2O \Rightarrow C_3A{\cdot}3CaSO_4{\cdot}32H+2AH_3$
$3CA+9C\$+6CH+90H \Rightarrow 3C_3A{\cdot}3CaSO_4{\cdot}32H$
OPC+CAC+C$, CAH–CSH system
$CA+C+H_2O \Rightarrow C_4AH_{13}$
$CA+10H_2O \Rightarrow CAH_{10}$
$C_3S+H_2O \Rightarrow C\text{–}S\text{–}H$

The formulations A to C belong to the region of ettringite system and the formulations D to G belong to the region of CAH–CSH system [1,3]. Within the ettringite or CSH–CAH system the mineral composition was mostly kept constant. Major modifications in properties were achieved by modifying admixture type and amounts. The combinations of raw materials for SLUs A to E were mixed before the corresponding experiments, whereas, the two formulations F and G were used as a premixed dry mortar provided by Degussa Construction Polymers GmbH. The Melflux plasticizers are polycarboxylate ether type plasticizers (PCEs).

2.2. Method

Measurement of workability, setting time, viscosity, and hydration kinetics through calorimetry was performed for each formulation.

2.2.1. Workability and setting time

Flow test as an index of fluidity was measured by based on EN 12706 and a flow cone specified by JIS R 5201. The measurements were started immediately after mixing. The spread width of the SLU on a flow plate was measured without drops.

Set test was measured based on EN 196–3.

2.2.2. Rheology

Viscosity tests were performed using a Haake RheoStress 150 from Thermo Electron Corporation with a profiled, concentric-cylinder system. Rotational viscosity at shear rates of 15 (1/s) and 30 (1/s), respectively, was measured as a function of time. Moreover, shear rate with increasing shear stress from 0 to 50 Pa was continuously measured. The yield stress was calculated from the obtained curve. However, a yield stress could not be measured for B1.

2.2.3. Hydration kinetics

Calorimetric tests as an index of hydration kinetics was measured by using the conduction calorimeter of a triple type. The evolution of heat of hydration was monitored for one day. Moreover, for formulation E, the influence on the rate of heat evolution by different combinations of admixtures (an accelerator, a retarder, a plasticizer) was also investigated.

The heat evolution curve for a typical Portland cement paste, determined by conduction calorimetry is shown in Fig. 1 [4]. According to H. F. W. Taylor, the process may be divided into five stages for the initial reaction, the induction period, the

Table 2
Formulations of SLU

		Ettringite system					CAH–CSH system			
		A1	A2	B1	B2	C	D	E	F	G
Materials (%)										
Ciment Fondu Lafarge		20	20	20	20	20	8	12	12	12
Cement CEM I 42.5 R		4	4	4	4	4	16	19	19	19
Hemi-hydrate alpha		7	7	7	7	7				
Anhydrite							4	7	7	7
Quartz sand (0.2–0.5 mm)		38	38	38	38	38	39	41	41	41
Fine grained limestone		28	28	28	28	28	31	20	20	20
Redispersible powder		2	2	2	2	3	2	2	2	2
Admixture (%)										
Plasticizer	Melflux PP100F	0.20								
	Melflux 2651F		0.20				0.20	0.20	0.20	
	Melflux 1641F			0.30	0.30					
	Casein					0.20				0.40
Accelerator	Lithium carbonate	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
	Sodium bicarbonate					0.20				
Retarder	Citric acid	0.02	0.02	0.02			0.12	0.20	0.20	0.20
	Tartaric acid				0.02					
	Sodium citrate					0.20				
Stabilizer	Cellulose ether	0.05	0.05	0.05	0.05	0.05	0.05	0.05		0.10
	Starvis VP0005								0.20	
Casein activator	Calcium hydroxide					0.40				
Shrinkage reducer	Neopentylglycol								0.60	0.60
Defoamer									0.30	0.30
Water powder ratio		0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.20	0.20

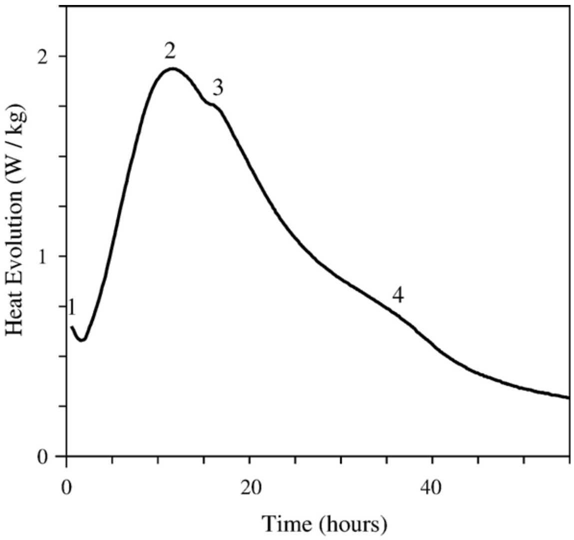

Fig. 1. Rate of heat evolution at 20 °C for a typical Portland cement [4].

acceleratory period, the deceleratory period and the final period of slow reaction. Periods one and two correspond to the early stage of reaction, periods three and four to the middle stage, and period five to the late stage. The initial peak (1) can be attributed to a combination of exothermic wetting and early-stage reactions, which give a gelatinous coating and rods of AFt phase on cement grains. Rehydration of hemi hydrate to give gypsum may contribute. The main peak (2) corresponds to middle-stage reaction, in which the main products are C–S–H and CH. The gradually decreasing rate of heat evolution after 24 h corresponds to the continuing slow reactions of the late stage, which again give mainly C–S–H and CH. Many cements show a shoulder or an even more defined peak (3) at about 16 h. It is associated with renewed formation of ettringite. A further, less distinct shoulder (4) has been associated with hydration of the ferrite phase or conversion of AFt to AFm phase.

2.2.4. Ageing of dry mixture

The influence of ageing on viscosity and the rate of heat evolution for the formulation A1 have been measured. Three samples which were fresh SLU, cured SLU in the air of 20C, R.H.65% for 48 hours after mixing and sealed SLU in the glass container for 48 h after mixing were used for measurement. The sample of sealed SLU for calorimetric test was sealed for 72 h.

3. Results

3.1. Workability and setting time

The flow value and setting time which were obtained for each formulation are shown in Table 3.

3.1.1. Ettringite system

About flow ability, A2 with MF 2651F as plasticizer exceeded A1 with MF PP100F. MF 1641F used by B1 shows a smaller effect than MF PP100F, in spite of having been added mostly. However, setting time is the slowest when MF PP100F is used.

Table 3
Flow value and setting time

Formulation		Flow value (cm)	Setting time (hh:mm)	
			Initial	Final
Ettringite system	A1	25.9	0:45	0:49
	A2	38.4	0:28	0:31
	B1	23.4	0:30	0:33
	B2	29.9	0:37	0:41
	C	38.7	1:15	1:26
CAH–CSH system	D	38.9	1:27	1:48
	E	38.5	1:46	2:11
	F	39.5	1:54	2:15
	G	35.0	2:22	3:11

For the retarder, tartaric acid used by B2 turn out being more effective for a thinning than citric acid used by B1. Further, in case A2, when the amount of citric acid is increased from 0.02% to 0.1%, the flow value decreases to 78%. Then, when the amount of citric acid is increased from 0.02% to 0.2%, the flow value increases to 105%.

In case of C with casein as plasticizer, the good flow value is obtained by adding tri-sodium citrate at 0.2%. When the amount of tri-sodium citrate is decreased from 0.2% to 0.15%, the flow value hardly changes. However, the material stiffens at the time of mixing with water when the amount of tri-sodium citrate is reduced from 0.2% to 0.05%. Moreover, compared with other formulations in the ettringite system, setting time is greatly delayed by influence of an increase of the amount of tri-sodium citrate.

3.1.2. CAH–CSH system

In case of D, the good flow value is obtained at 0.12% of citric acid addition. E is based on the mix design of F. Although water powder ratios differ, a flow value and a setting time

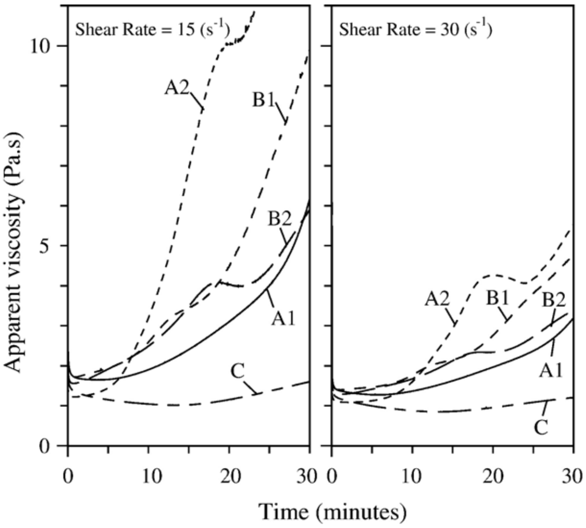

Fig. 2. Apparent viscosity as a function of time, ettringite system.

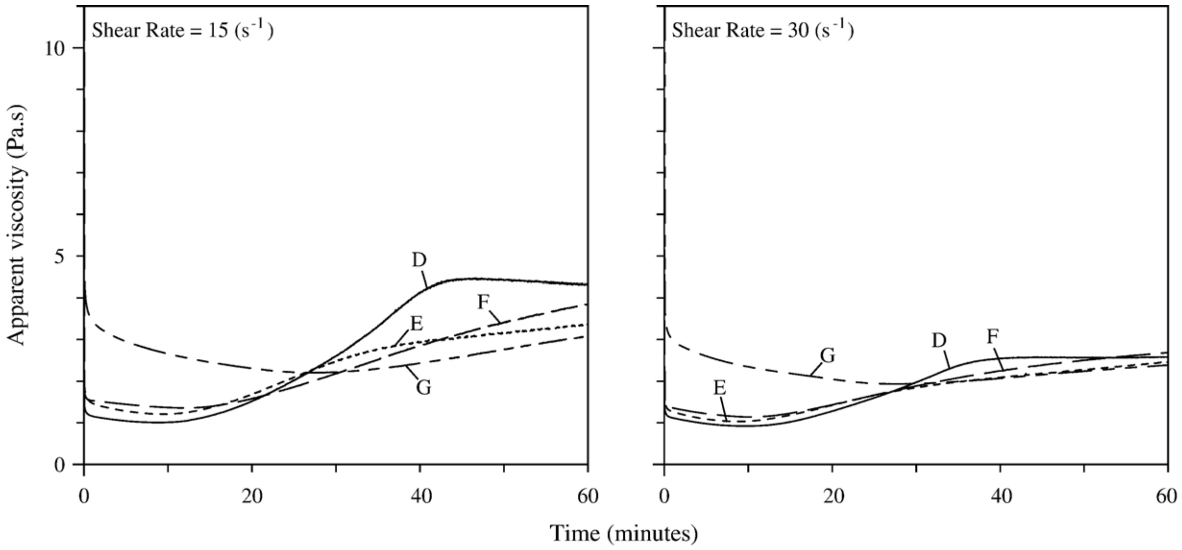

Fig. 3. Apparent viscosity as a function of time, CAH–CSH system.

almost equivalent to F are obtained at 0.05% of cellulose ether. When the amount of citric acid in E is decreased from 0.2% to 0.1%, the flow value decreases to 93%. Then when the amount of citric acid is decreased from 0.2% to 0.02%, the material stiffens at the time of mixing with water. By using hemi hydrate instead of anhydrite, since this system is a low amount of CAC, before dissolution of CAC occurred, sulfate ions enter quickly into the solution, block that reaction by migrating to the surface of C3A in cement, and are considered that it may not be able to stiffen [5]. However, it is not easy to adjust so that flow ability may be improved by a short open time. In the case of the short open time, rapid set mortar, tile adhesives, repair mortar, etc. are suitable by this system [1]. The kind and amount of a plasticizer and a stabilizer differ between F and G. The flow value of G is smaller than that of F although the dosage of plasticizer is twice the amount of F and the dosage of stabilizer is 0.5 times the amount of F. Moreover, the setting time of G is later than that of F.

3.2. Rheology

The apparent viscosity as a function of time for the ettringite system is shown in Fig. 2. When the shear rate is increased from 15(1/s) to 30(1/s), the absolute values of viscosity are decreased. However, increasing apparent viscosity as a function of time is observed for all formulations independent of the share rate. Moreover, it is observed that the viscosity of every formulation once falls from immediately after the start of the measurement, rises again after that, and shows a local minimum. A2, B1 and B2 show it about after 1 min and A1 shows it about after 5 min and C shows it about after 15 min. Within 30 min, it is observed that A2, B1, and B2 show a 2nd local minimum. However, the 2nd local minimum of B1 is not clearer than that of B2. And then the slope of increasing viscosity is proportional generally in order of the set start. In case of C with late setting time, the viscosity begins to rise about 15 min after start of a measurement.

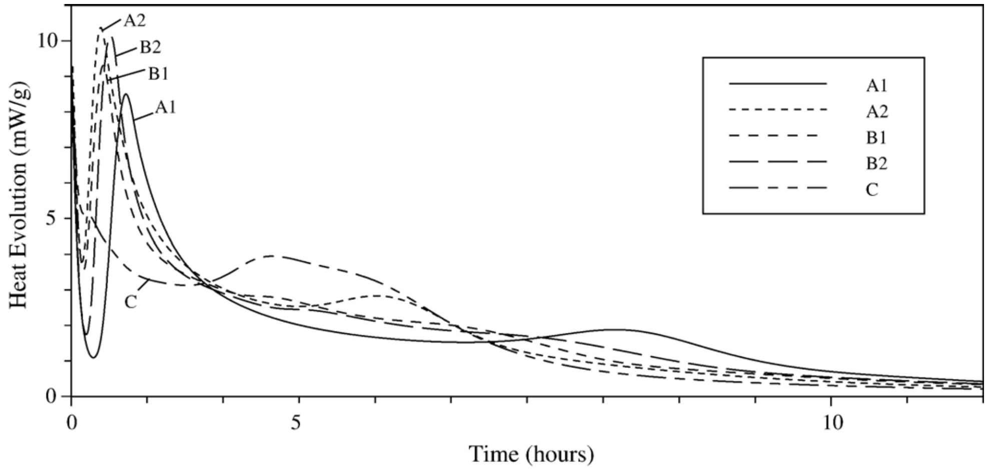

Fig. 4. Rate of heat evolution as a function of time, ettringite system.

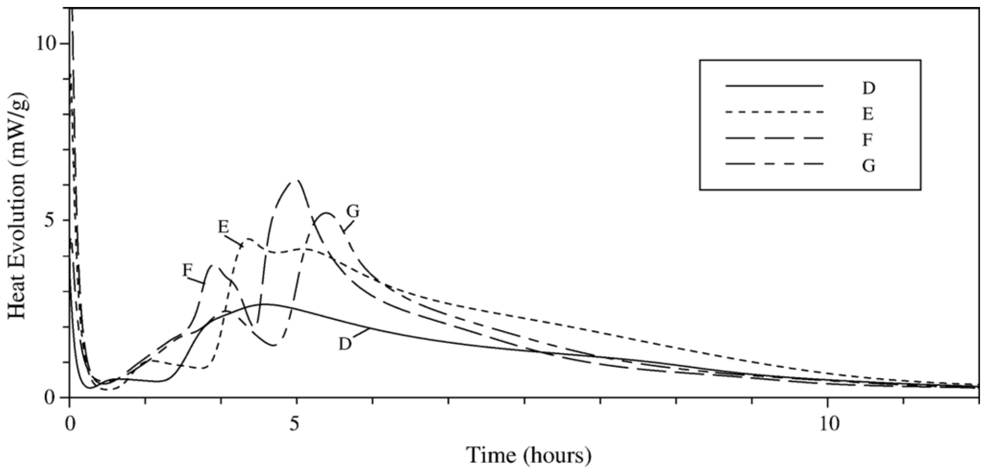

Fig. 5. Rate of heat evolution as a function of time, CAH–CSH system.

The apparent viscosity as a function of time in CAH–CSH system is shown in Fig. 3. The same tendency as for the ettringite system is observed, when the shear rate is increased form 15(1/s) to 30(1/s), the apparent viscosity decreases. Also, the tendency of increasing viscosity as a function of time is the same. However, the increase of viscosity is much less pronounced as compared to the ettringite system because of late setting time. D, E and F show the local minimum about after 10 min and G shows it about 30 min after the start of the measurement. Moreover, the viscosity of D falls a little about 40 min after the start of the measurement.

3.3. Hydration kinetics

The rate of heat evolution curves as a function of time for the ettringite system is shown in Fig. 4. In the case of A series, two exothermic peaks are observed after the short induction period. Comparing A1 and A2, the 1st and 2nd peaks with A2 occur earlier than that of A1, respectively. For the B series, unlike A series, one pronounced exothermic peak followed by two weak exothermic peaks are observed. The difference between the two series can either be explained by the type or dosage of plasticizer. Moreover, all peaks of B2 are observed slightly later than that of B1, probably due to the difference in retarder.

The rate of heat evolution of C differs from the other formulation. The heat evolution shows neither a clear induction period nor a pronounced first peak. C shows a heat evolution higher than the CAH systems (Fig. 5).

The rate of heat evolution curves as a function of time in CAH–CSH system is shown in Fig. 5. The induction period is longer than for the ettringite systems as it is also observed for the setting times.

In case of D, the area of the peak after an induction period is small compared with the other formulations. It is thought to be caused by less binder than for the other formulations. Although the setting time of E and F is almost equivalent, the heat evolution curves differ, what the first peak is concerned. Moreover, although the first peaks in the heat evolution curves of F and G are equivalent, the second heat evolution peak of G is delayed in accordance with setting time.

In Fig. 6, the influence of admixture combinations (accelerator, retarder, and plasticizer) on the rate of heat

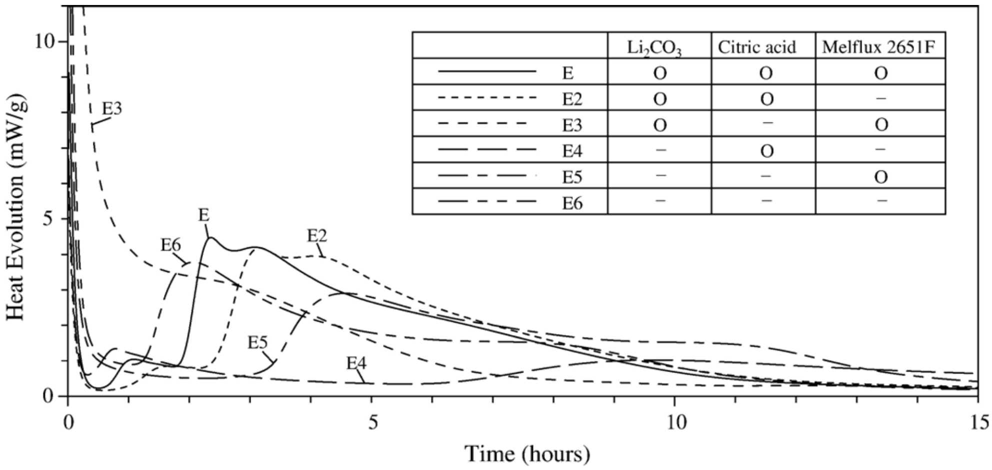

Fig. 6. Rate of heat evolution according to the combination of admixtures.

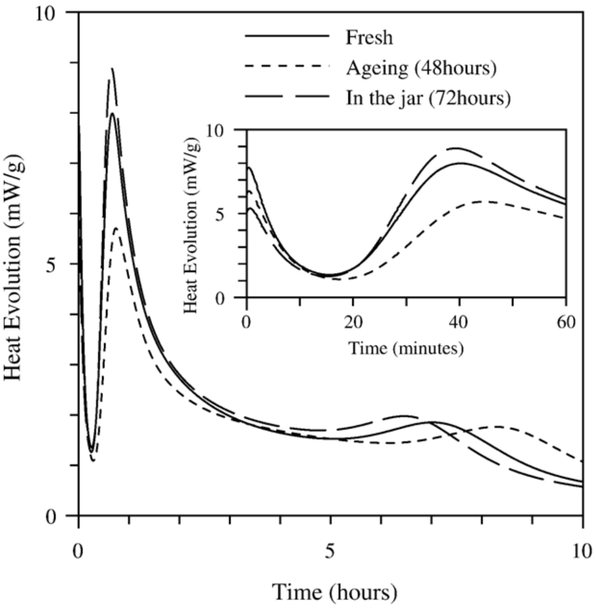

Fig. 7. Influence on rate of heat evolution by ageing.

evolution is shown for formulation E. In case of E6 with no admixtures, the peaks after the induction period are observed after about 2 h and about 8 h. In case of E5 which added only the plasticizer, the induction period becomes long and the peaks are observed after about 4.5 h and about 11 h. The hydration is delayed by using the plasticizer for about 3 h. In case of E4 with only the retarder added, an individual small peak at 0.7 h is observed first. Then, the induction period continues for a long time, and a broad peak is observed after around 10 h. In case of E2 with accelerator and retarder, a small peak considered to be due to the retarder is observed after 1.5 h. Then, the peaks are observed after about 3 h and about 4 h. In case of E3 with accelerator and plasticizer, a pronounced heat evolution is observed immediately after mixing, and an induction period is not able to be seen. In case of E with all admixtures added, a small peak considered to be due to a retarder after about 1 hour is observed, two other peaks being observed after about 2.4 h and 3 h. Moreover, the slope of the 2nd peak is steeper than for the other formulations. The peak when adding only the retarder is behind compared with the case where accelerator and retarder are combined added. However, this peak starts even earlier when combining accelerator, retarder, and plasticizer. This is considered to relate to heat evolution having become early and sharply when accelerator and retarder are combined. The results show that the combination of admixtures allows controlling setting time and hydration rate.

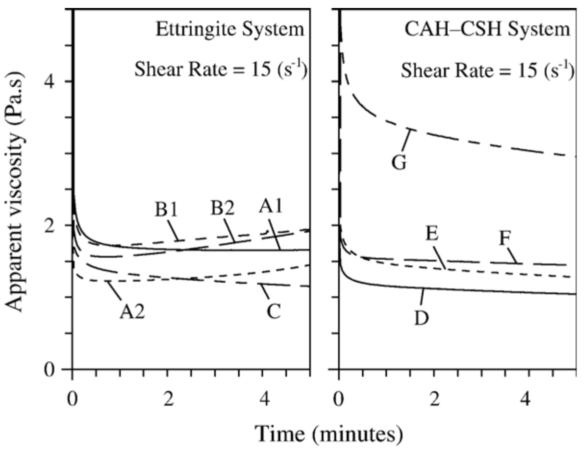

Fig. 8. Apparent viscosity as a function of time (early period).

Further, the influence of ageing on the rate of heat evolution is shown in Fig. 7. The first peak in the heat evolution curve of the aged sample is a little delayed as compared to the fresh sample, and the sealed sample. Furthermore, the peak area also decreases. Moreover, the 2nd peak of the aged sample is further delayed. This result shows clearly that the rate of heat evolution is delayed by ageing.

4. Discussion

4.1. Flow and rheology

The apparent viscosity shortly after mixing is shown in Fig. 8. In the ettringite system, when the apparent viscosity at 1 minute after the start of the measurement is compared, MF 2651F and tartaric acid contribute to a low viscosity. A1 and B1 are at slightly higher and equivalent viscosities. A correlation with the flow value, however, could not be recognized. Similarly, in the CAH–CSH system that correlation was not recognized. Particularly, the viscosity of G is large considering the flow value.

Then, attention was paid to the relation of yield stress and flow value instead of viscosity and flow value. As shown in Fig. 9, a correlation was obtained between the yield stress and

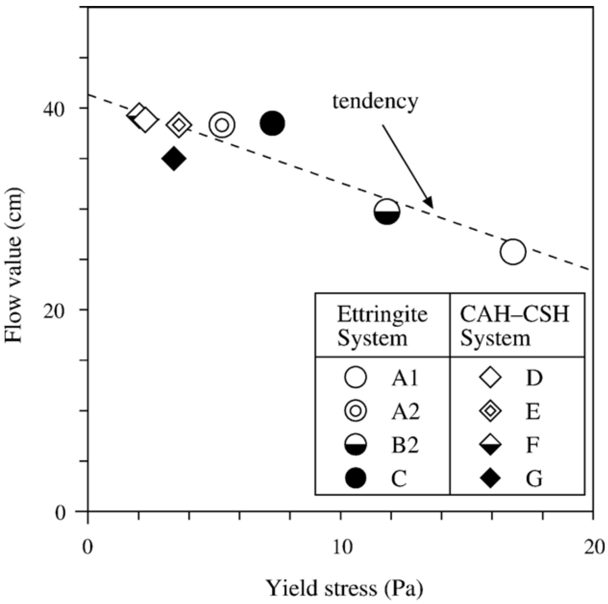

Fig. 9. Correlation between yield stress and flow value.

the flow value. When the yield stress is small, the flow value becomes large, when the yield stress is large; the flow value becomes small, showing an inverse proportionality. Similar relationships have been reported for concrete by Ferraris et al. [6]. Nevertheless, C and G with casein as plasticizer separate from the tendency a little.

For the case in which the yield stress is small and in which a flow value is large, it is thought that the particles in the state of aggregated structure of SLU is easy to break and is hard to reconstruct. It seems that the adsorbed plasticizer and/or retarder reduce particle interaction forces thus contributing to the phenomenon. Moreover, it seems that viscosity is correlated to the rate of flow until the SLU reconstructs an aggregated structure since it is observed that the speed with which the SLU spreads changes with formulation.

4.2. Calorimetry and rheology

4.2.1. Ettringite system

The rate of heat evolution curves as a function of time during the first hour is shown in Fig. 10. The order of appearance of the 1st peak after the induction period in each formulation is proportional to setting time. Although it is generally accepted that the setting time is located at the acceleratory period of a heat evolution curve, the setting time in these experiments is located in the deceleratory part of the peak. This holds true except of formulation C. It is thought that the time lag occurs because the hydration rate of these formulations is quite quick compared to ordinary cement. The induction period of A2 with MF 2651F is shorter than that of A1 which used MF PP100F showing the same trend as the setting times. Because MF 2651F is also excellent in flow ability, it is thought that this plasticizer has long side chains compared with MF PP100F. And then although there is a higher amount of MF 1641F added than MF 2651F, the extension of the induction period is small. It seems that the structure of MF 1641F resembles to MF 2651F from this. However, because the contribution to flow ability is a little less, it is considered that the side chain is shorter than MF 2651F.

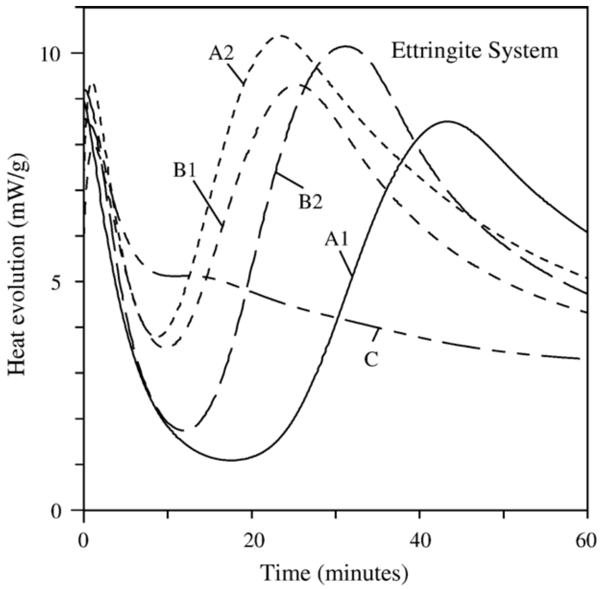

Fig. 10. Rate of heat evolution (early period).

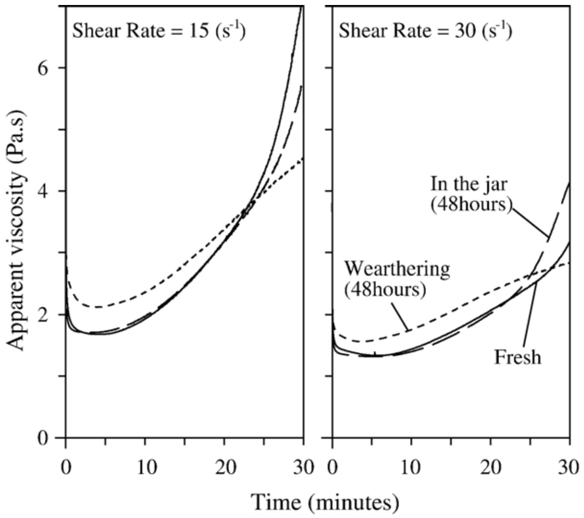

Fig. 11. Influence on the viscosity by weathering.

The induction period of B2 with tartaric acid is longer than that of B1 with citric acid showing the same trend as for the setting times.

As compared with the result of the viscosity of Fig. 2, the 1st local minimum of viscosity is earlier than the end of the induction period in heat evolution curves for all formulations. It is considered that this local minimum represents a stable zone where the aggregated structure of particles is being destroyed by shear stress. And it seems that viscosity will rise again when hydration progresses and the bonding strength between particles increases. Comparing A2 with A1, the viscosity of A2 with MF 2651F rises early as well as the setting time and the rate of heat evolution. Comparing B1 with B2, the increase in viscosity in the first half is equivalent, but later the viscosity of B2 is larger than B1 (second local minimum). A2, B1, and B2 show a 2nd local minimum within 30 min. It is considered that this is related to the first peak of the heat evolution curve.

4.2.2. CAH–CSH system

When the result of the rate of heat evolution of Fig. 5 is compared with setting time, the setting times of D and E correspond to the acceleratory period of the heat evolution curve, but F and G are not in agreement. It is thought that that the double peak in the heat-evolution curve of F and G is an indication for this behavior or the acceleratory period can not be determined in the same way.

Moreover, as compared with the viscosity of Fig. 3, the behavior of rate of heat evolution curve for 60 minutes and viscosity curve is comparatively the similar in D and G. Although there are many dosages of casein when F and G are compared, the early viscosity is large, and the flow value is small. In the case of CAH–CSH system at low water powder ratios, it is considered that it is better to use MF 2651F of polycarboxylate ether.

4.2.3. Ageing of dry mixture

The influence of ageing on viscosity is shown in Fig. 11. For both shear rates, the aged sample shows high viscosity from immediately after start of the measurement. However, after 25 min the viscosity curve of the aged sample is crossed by the viscosity curve of the samples which are not aged. This seems to be an indication that the kinetics of hydration is slowed down for the aged sample. Correspondingly, the slope of a rate of heat evolution curve is smaller after 20 min (see Fig. 7). The inversion of the viscosity behavior is in line with this result.

As a mechanism of ageing, the following things are mainly known. Reactive sites in calcium aluminate and calcium silicate phases in CAC and OPC react with CO_2 and H_2O from the air and form phases which might be close to hydrate phases and carbonate. Thus the surface of cement particles is covered and the cover can act either as a diffusion barrier or prevent organic molecules such as plasticizers to adsorb on the surface. As a cause the viscosity is high from immediately after mixing because the plasticizer can not adsorb on the particles and contributes by dissolution in water to the increase in viscosity.

Moreover, for the same reasons hydration becomes late, since the surface of a cement particle is covered with $CaCO_3$, hydrate like phases etc.; this means that the reactivity of the hydraulic compounds in cement decreases. What the influence of ageing on the physical properties is concerned, the reduction in slump (required increase in amount of water) and its strong decrease are known for concrete. For the SLUs, further experiments are needed.

4.2.4. Practical considerations

Finally, the ettringite system is suitable in cases where a short open time and good flowability are required. Particularly, the combination of MF 2651F and citric acid is good. And, it is considered possible to use tartaric acid instead of citric acid. The CAH–CSH system is suitable in cases where a long open time is required. Moreover, it is possible to have extended open time, keeping flowability on a constant level by increasing a retarder addition in the ettringite system. Moreover, this system not only can be adjusted to long open time, but allow at the same time a very rapid use after application [3]. From now on, it is necessary to investigate succeedingly physical properties, such as dimensional stability and a development on the strength, about the application to SLU in these formulations. Although the casein (it has separation resistance and smoothes the surface of SLU well) currently used in Europe was also examined a little, hydration was influenced sensibly and it is thought that handling may be difficult. It seems that there are also various problems and the substitution to polycarboxylate ether is progressing.

5. Conclusion

This study investigated the influence of raw materials on the properties such as workability, rheology and hydration kinetics in SLU based on CAC–OPC–C$. The obtained conclusions are shown below.

1. Flow behavior is mostly influenced by the type of plasticizer and PCE are very efficient. MF 2651F showed the most pronounced effect on flow ability, followed by MF PP100, and last MF 1641F. The retarder also contributed to a thinning and tartaric acid performed in general better than citric acid.
2. The plasticizer also retards hydration, especially MF PP100. Tartaric acid contributed stronger than citric acid to the effect of retardation.
3. The effects of plasticizer and retarder can be studied by rheological and hydration measurements. Like other cementitious systems, SLUs show shear thinning and an increase in apparent viscosity when major hydrates are formed.
4. Although a correlation was not found between a flow value and viscosity, an inverse proportional correlation exists between flow value and yield stress.
5. The ettringite system is suitable in cases where a short open time and good flowability are required. The CAH–CSH system is suitable in cases where a long open time is required. Moreover, it is possible to have an extended open time, keeping flow ability on a constant level by increasing the retarder addition in the ettringite system.

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