

Cement – Superplasticizer Incompatibility: Hydration Products Involved In Rheological Changes

EDWIGE NICOLAS, DANIELE WALDMANN, MANFRED GREGER, CECILE DILIBERTO,
ANDRE LECOMTE, BERNARD MALAMAN, GUY SCHARFE, CARLO KIRPACH

Concrete Laboratory, F.S.T.C, University of Luxembourg
6, rue Richard Coudenhove-Kalergi, L-1359 Luxembourg, Luxembourg
edwige.nicolas@uni.lu

Abstract

Most modern concrete structures integrate superplasticizer in their formulations. The last generation polycarboxylate-type products present a great efficiency at short interval. But, in few cases, the plasticity is not maintained with the time due to incompatibility reasons between aggregates, binder and superplasticizer.

These phenomena are highlighted by rheological tests easy to implement. The stiffening is assessed on paste by the Tousshenbroeck's test (adapted to EN 196-2 standard), which used the Vicat's apparatus. Various workability tests were performed using different combinations of cement paste and superplasticizer. The set results allow distinguishing comparison between compatible and incompatible mixes.

The study of the flow behaviour of different mixes is deepened by the use of a rheometer equipped with an original measuring system composed of an eccentrically rotating sphere. The Bingham's curves, characteristic of cement particle suspensions, may be established for different formulations. Yield stress and plastic viscosity are then calculated. It appears that these values are influenced by several parameters including especially superplasticizer addition and time of hydration.

By stopping hydration process of cement mixes, mineralogical composition of these systems can thus be studied by different analytical techniques of solid state chemistry (XRD, SEM...). Chemically, consistency of these cement mixes can be related to the formation of ettringite ($\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$), which is formed in excess and/or with needle-like shape.

1. Introduction

Most modern concretes incorporate superplasticizers into their formulation. These "deflocculating" products are intended to improve the concrete workability without an excess of water. More compact and less permeable concretes, which have usually a water/binder ratio less than 0.50, are thus achieved.

Superplasticizer is part of admixtures which are able to modify the rheological properties of fresh concrete. This product improves the fluidity of concrete by dispersing cement particles in paste. High-performance concrete including high-strength one can be produced with superplasticizer by reducing water/cement (w/c) ratio of cement paste, mortar and concrete without significantly changing their flow properties. The last generation polycarboxylate-type products show a great efficiency at short term. But, in some few cases, plasticity is not

maintained with the time due to incompatibility reasons between aggregates, binder and superplasticizer.

Workability is the property of freshly mixed concrete or mortar that determines the ease and partly the homogeneity, with which it can be mixed, placed, consolidated and finished¹. It often contains a part of subjectivity with regard to the ability of concrete to be transported, pumped and placed, to flow and to segregate, to have a good consistency and stability². Several testing devices are used in practice to measure workability like slump or slump flow tests. But the values obtained from these measurements should be considered with care, because they do not fully characterize the flow behaviour. Rheometers give a better insight into the flow behaviour of cement materials because they provide fundamental rheological values, which are the yield stress and plastic viscosity, and they also allow to draw flow curves, which are characteristic of various flow behaviours. Therefore they are very helpful devices for optimizing the mix design and provide precise results.

The cement / superplasticizer interactions are complex processes. Actually, Portland cements are multi-phasic inorganic materials, comprising major components (C_3S , C_2S , C_3A , C_4AF) and minor phases ($CaSO_4 \cdot xH_2O$, CaO , $(Na,K)_2SO_4$, etc.). The same goes for the organic admixtures, which often contain several components owing to the product's nature or to the result of their manufacturing process³.

The purpose of this paper is to determine and interpret the rheological behaviour of cement pastes incorporating or not superplasticizer. For that, an original measuring system is used, namely the ball measuring system⁴. Firstly, the influence of hydration time and superplasticizer addition on the rheological values of different mixes will be examined. Finally, two incompatibility cases will be studied on rheological and chemical point of view.

2. Materials and Testing Details

2.1 Materials

Three different commercial Ordinary Portland Cements and an artificially produced cement with a small dosage of calcium sulphate have been used for the tests on pastes. They consist in:

- a cement CEM I 42,5 R (cement A),
- a cement CEM I 42,5 R with a small dosage of calcium sulphate (cement B),
- two cement CEM I 52,5 R (cement C and D).

Admixtures chosen are three commercial products named SP1, SP2 and SP3. They are based on aqueous solutions of polycarboxylate-type superplasticizers usually used by the concrete producers.

2.2 Cement paste testing details

2.2.1 Workability characterization

The Van Toussebroeck's test (adapted to the EN 196-2 standard) is used for the stiffening intensity evaluation of cement pastes. This measurement is carried out on mixtures whose w/c ratio is 0,35. Superplasticizer content is 0,3% compared to the cement mass and is referring to the aqueous solution and not to the solid fraction. The cement paste is mixed for 15 seconds at low

speed (140 rpm) and for 45 seconds at high speed (285 rpm). The penetration of the Vicat's consistency probe is measured at 3, 5, 7, 10 and 15 minutes after starting mixing.

2.2.2 Rheometrical measurements

The flow behaviour of cement paste, mortar and concrete can be in many cases described with sufficient accuracy by the Bingham model:

$$\tau = \tau_0 + \eta_{pl} \cdot \dot{\gamma} \quad (1)$$

where : τ = shear stress,
 τ_0 = yield stress,
 η_{pl} = plastic viscosity,
 $\dot{\gamma}$ = shear rate.

The physical interpretation of the yield stress is that a minimum stress has to be applied to the material in order to start flowing. Above the yield stress, shear stress vs. shear rate curve has a constant slope that is generally termed as plastic viscosity η_{pl} .

Flow curves of the pastes were measured by the use of a rheometer Paar Physica UDS 200⁴ equipped with a ball measuring system (BMS). This system has been developed by Müller et al.⁵ especially for cement pastes and mortars.

The measuring principle is shown in Figure 1. Instead of a laminar flow, as in other geometries like plate-plate or cylinder, a displacement flow is caused by an eccentrically rotating sphere⁶. The sphere moves in the paste at a sufficient distance of container wall so that the flow of the paste was not under its influence. During this movement, the speed of the sphere is constant and torque is measured.

According to Tyrach⁷, the governing equations of the ball measurement system are as follows.

The movement of a sphere through a Newtonian fluid for Reynolds number $Re < 1$ can be expressed by the Stokes equation, assuming that the Stokes equation is also valid in the case of a non-Newtonian medium like cement paste:

$$F = 3 \cdot \pi \cdot \eta \cdot v \cdot D \quad (2)$$

where : F = force,
 η = dynamic viscosity of the fluid,
 v the velocity of the sphere,
 D = the diameter of the sphere.

The Reynolds number is defined as:

$$Re = \frac{v \cdot D \cdot \rho}{\eta} \quad (3)$$

where Re = Reynolds number,
 ρ = fluid density.

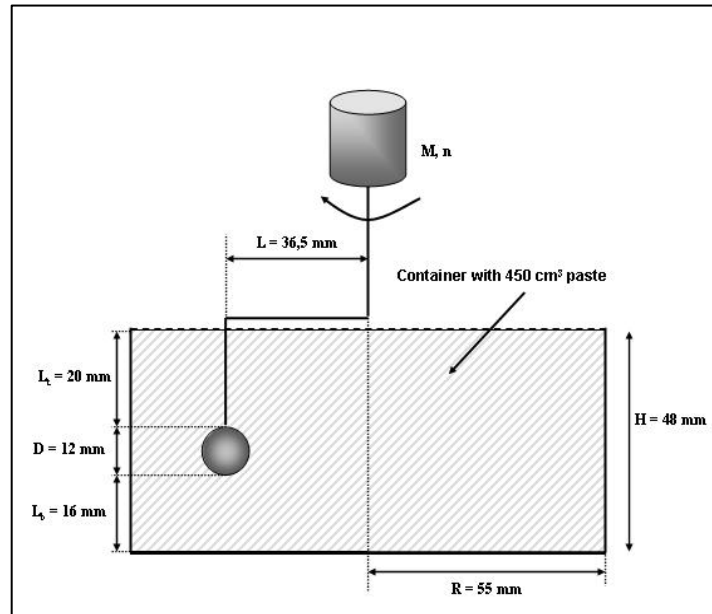


Figure 1: Principle of a rheometer with a sphere measuring system according to Tyrach⁷ and influential geometrical parameters.

Torque and sphere velocity are given as:

$$M = F \cdot L \quad (4)$$

$$v = 2\pi \cdot n \cdot L \quad (5)$$

where M = torque,

L = distance between sphere and container centre,

n = number of rotations by time unit.

From previous equations, rotational torque can be established. An additional torque, which results from the self-rotation of the sphere, must be added in order to obtain the total torque measured by the rheometer. Finally, by application of the dynamic viscosity definition, linear relationships, between shear rate and number of rotations by time unit on the one hand, and between shear stress and torque on the other hand, appear as it is shown in equations (6) and (7).

$$\dot{\gamma} = K_{\dot{\gamma}} \cdot n \quad (6)$$

$$\tau = K_{\tau} \cdot M \quad (7)$$

The proportionality factors are related to the geometry of the system: influence of the thin ball holder, container wall and bottom, and diameter of the sphere.

Experimental problems are encountered because of the studied cement pastes consistency. At first, a material modification occurs in the area of the sphere penetration. It is then necessary that the ball covers a certain distance before beginning the measurement so as to leave this perturbation domain. Then a material accumulation in front of the sphere is produced by the progression of the ball through the paste. So the sphere must be introduced for each measurement

in a new material. It should be noted that these experimental conditions are borderline cases of this measurement system. But the experiments are yet led to know if its use is still valid.

The rheological behaviour of mixes is determined at 5, 10 and 15 minutes by linear regression and extrapolation of obtained fit.

2.3 Chemical analysis

The hydration of cement paste is stopped by immersion of the suspensions in acetone. The collected solid phases are subjected to several tests of solid state chemistry.

Anhydrous or hydrated crystallized phases are characterized by X-ray diffraction (XRD).

The microstructure of hydrated pastes was observed by scanning electron microscopy (SEM).

3. Results

3.1 Influence of hydration time and superplasticizer use on compatible mixes

Flow curves are determined for cement A and cement B pastes, in presence or not of superplasticizer 1 and superplasticizer 2. It should be noted that these pastes show very weak stiffening according to Van Tousshenbroeck's test. As an example, the Bingham's curves of cement B paste in presence of SP2 at different times of hydration are presented in Figure 2. Similar graphics are obtained for the other studied cement pastes. Fundamental rheological values and stiffening measurements of the four mixes are gathered in Table 1.

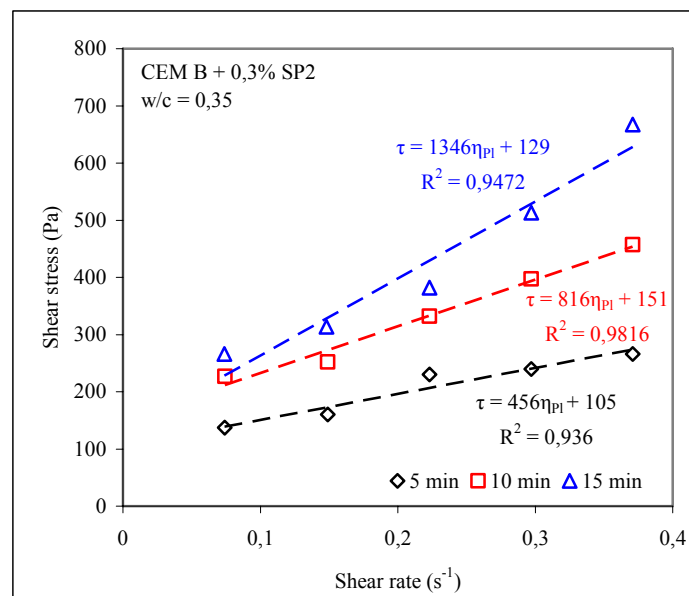


Figure 2: Flow curves of cement B paste with SP2 at different time of hydration

Table 1: Fundamental rheological values and stiffenings of cement A and cement B pastes
(w/c = 0.35 ; SP = 0.3%)

Paste n°: made with :	Time hydration (min)	τ_0 (Pa)	η_{pl} (Pa.s)	Penetration (mm)	Toushenbroeck's Stiffening
1 :cement A	5	86	661	39	very weak
	10	70	1480	39	very weak
	15	124	1361	37	very weak
2 :cement A + SP1	5	120	1108	38	very weak
	10	269	2054	30	very weak
	15	343	2725	28	very weak
3 :cement B	5	47	334	40	very weak
	10	75	413	39	very weak
	15	57	548	37	very weak
4 :cement B + SP1	5	84	303	40	very weak
	10	98	404	39	very weak
	15	104	438	37	very weak
5 :cement B + SP2	5	105	456	36	very weak
	10	151	816	32	very weak
	15	129	1346	26	very weak

Considering the hydration time influence, it appears that yield stress and plastic viscosity increase with hydration time. But plastic viscosity increase is greater than the yield stress one. Indeed, the measured yield stress values for a same paste have a similar order of size in the observed time domain; nevertheless an increasing inclination emerges from these measurements. On the other hand, the determined plastic viscosity values increase clearly with hydration time.

Therefore, small increase of yield stress with the time is less pronounced under the effect of high rate of change of plastic viscosity from a workability point of view⁸.

The influence of superplasticizer addition on rheological properties of cement pastes is studied for cement B. If the values obtained for the paste 3 are compared to these measured for the pastes 4 and 5, different influences are revealed. Yield stress and plastic viscosity have a similar order of size between paste 3 and paste 4 when an increase of the rheological values is noted for the paste 5. Anterior tests on mortar's spreading⁹ with same materials could explain this observation. These measurements consisted in the determination of water content reduction allowed by incorporation of an increasing dosage of superplasticizer. They have shown that, small dosages, a water content reduction is possible by using SP2 even when SP1 has quite any action. This last superplasticizer have to be introduced at a dosage greater than 0,6% to produce a reduced water effect. The increase of yield stress and plastic viscosity observed from the paste 3 to the paste 5 could be linked to the decrease of Vicat's probe penetration into the paste. A similar trend is met in the cases of pastes 1 and 2. Weak stiffening of superplasticized paste is at the origin of yield stress and plastic viscosity increased. For same cement, a good correlation between rheological values and the penetration of Vicat's probe is obtained. But the evolution of plastic viscosity is sharper than the yield stress one. Therefore, paste consistency is mainly controlled by plastic viscosity in the considered superplasticizer dosage range.

So rheometrical measurements on these various pastes provide more information about the rheological behaviour than penetration measurements. Indeed different rheological properties are revealed, even when stiffening values are similar.

3.2 Cases of incompatibility

Two pastes presenting strong or very strong stiffening (corresponding to a penetration value less than 10 mm) are presented here. Chemical analyses were realised to explain the radical consistency change.

Firstly, rheological behaviour of cement C paste prepared with superplasticizer 3 is reported on Figure 3. Table 2 collect rheological values and stiffening measurements.

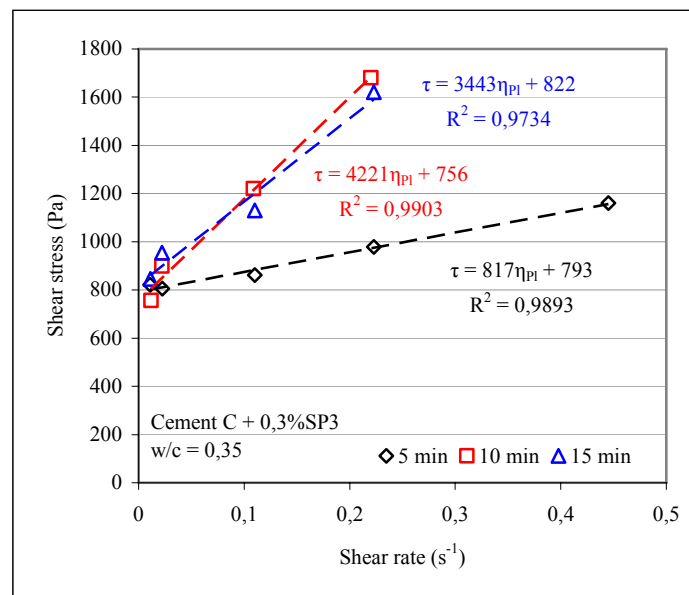


Figure 3: Flow curves of cement C paste at different hydration times

Table 2: Fundamental rheological values and stiffening of cement C paste (w/c = 0,35 ; SP3 = 0,3%)

Paste made with :	Time hydration (min)	τ_0 (Pa)	η_{pl} (Pa.s)	Toushenbroeck's penetration (mm)	Stiffening
cement C + SP3	5	793	817	18	Middle
	10	756	4221	9	Strong
	15	822	3443	9	Strong

Yield stress and plastic viscosity are clearly increased compared to the recorded values for previous pastes. The strong stiffening is at the origin of this great increase, and this, even for only five minutes of hydration.

Analyses by X-ray diffraction of anhydrous and hydrated cement C are shown in Figure 4. The anhydrous cement diffractogram reveals high aluminate phase C_3A content. This phase is known to be the more reactive of cement phases. Ettringite, hydration product of C_3A , appears

since the first minutes of cement hydration. By covering anhydrous cement grain, ettringite is at the origin of the induction period. During this time, a cement paste maintains a sufficient workability until to the set caused by the portlandite CH precipitation.

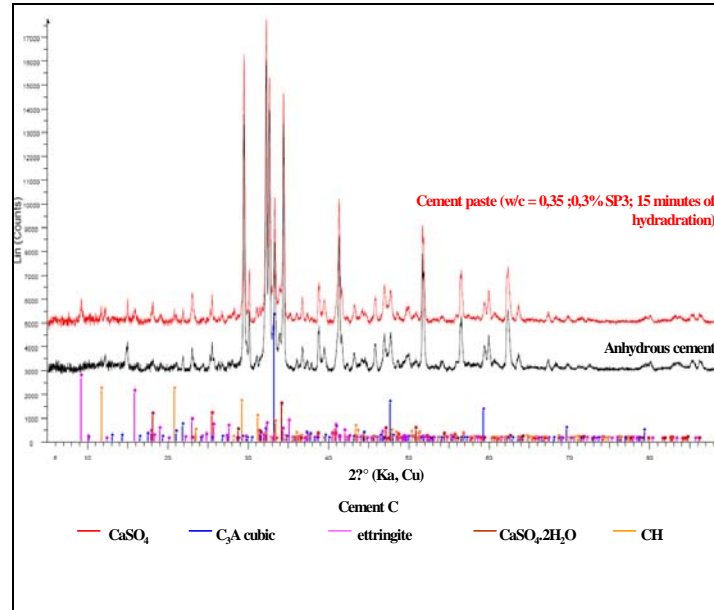


Figure 4: X-Ray diffractograms of anhydrous and hydrated cement C

Hydrated cement C diffractogram shows a significant quantity of ettringite and also reveals the presence of portlandite.

Therefore, at 15 minutes of hydration, this cement paste starts to set. Superplasticizer 3 has acted as an accelerator of set, and so led to the observed great rheological evolution.

Secondly, rheological behaviour of cement D paste incorporating 0,3% of superplasticizer 2 is studied. Stiffening values at different times of hydration are shown in Table 3. Rheometrical measurements are carried out only for 5 minutes of hydration because of the strong stiffening of the paste which prevents the ball measuring movement. The flow curve obtained is reported in Figure 5.

Table 3: Stiffening of cement D paste (w/c = 0,35; SP2 = 0,3%)

Time of hydration (min)	Toushenbroeck's penetration (mm)	Stiffening
5	7	Strong
10	6	Strong
15	5	Very strong

The flow curve of the paste does not correspond to a Bingham's behaviour. Indeed linear relationship between shear stress and shear rate is not verified. The recorded values obey to another known rheological behaviour: the Herschel-Bulkley model defined by the following equation:

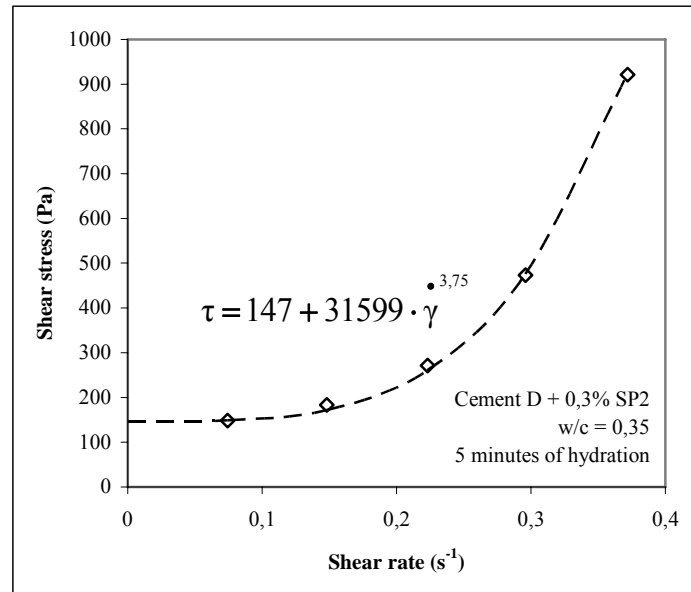


Figure 5: Flow curve of cement D paste

$$\tau = \tau_h + m \cdot \gamma^{p} \quad (8)$$

where τ_h = yield stress according Herschel – Buckley,
 m = flow coefficient,
 p = exponent.

As it is reported in Figure 5, yield stress of cement paste rises to 147 Pa. This order of size is closed to those of flowing pastes studied in the previous part. Therefore, stiffening is here characterized by a flow property change. The cement paste has in this case a dilating behaviour.

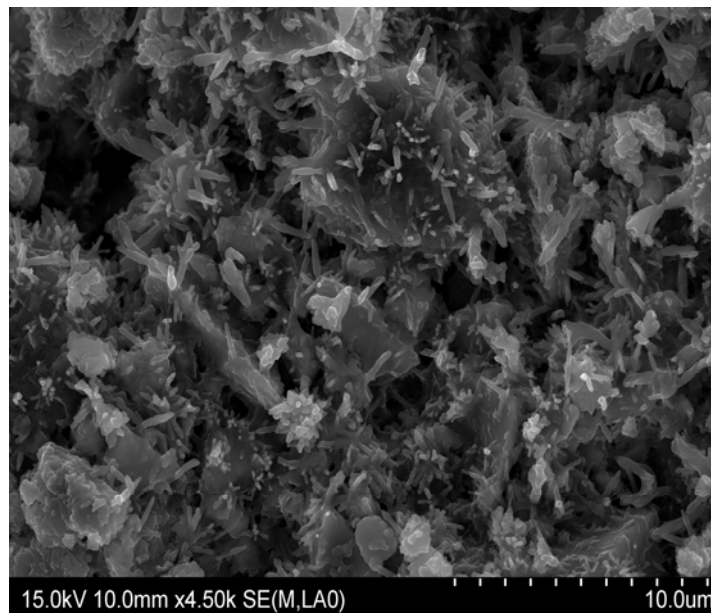


Figure 6: Scanning electron micrograph from cement D paste (w/c = 0,35 ; SP2 = 0,3% ; 15 minutes of hydration)

Scanning electron micrograph from this paste is shown in Figure 6. High density of ettringite with needle-like shape is observed on the cement grains surface. Frictions generated thus decrease plasticity of the suspension¹⁰.

4. Conclusion

The Ball Measuring System was used as a new rheometrical tool. Different cement pastes including or not superplasticizer were investigated.

During 15 minutes of hydration, yield stress and plastic viscosity increased with the time of hydration. Addition of superplasticizer led to a variation of rheological values when the dosage is sufficient. In the studied domain of time and superplasticizer dosage, paste consistency is mainly controlled by plastic viscosity and by yield stress in a less pronounced way.

Stiffening of cement paste was clearly underlined by order of size of the recorded rheological values or by the shape of the flow curve characteristic of flow properties (Bingham, Herschel-Buckley).

Consistency changes were linked with hydration products of cement as portlandite indicating the start of the set or needle-shape ettringite generating frictions between cement grains.

References

1. Neville A, Aitcin P.C. High performance concrete – An overview. *Materials and Structures* 1998, **31**:111-117.
2. Griesser A. Cement – superplasticizer interactions at ambient temperatures. *PhD thesis, Swiss Federal Institute of Technology, Zürich, Switzerland* 2002.
3. Jolicoeur C, Simard M.A. Chemical admixture – cement interactions: phenomenology and physico-chemical concepts. *Cement & Concrete Composites* 1998, **20**:87-101.
4. Rheometer Paar Physica UDS 200, www.paar-scientific.com.
5. Müller M, Tyrach J, Brunn PO. Rheological characterization of machine-applied plasters. *Zement-Kalk-Gips International* 1999; **52**:252-258.
6. Leeman A, Winnefeld F. The effect of viscosity agents on mortar and concrete. *Cement & Concrete Composites* 2007, **29**:341-349.
7. Tyrach J. Rheological characterization of cementitious building materials. *PhD thesis, University of Erlangen-Nürnberg, Germany* 1976.
8. Golaszewski J, Szwabowski J. Influence of superplasticizers on rheological behaviour of fresh cement mortars. *Cement and Concrete Research* 2004, **34**:235-248.
9. Nicolas E, Waldmann D, Lecomte A, Diliberto C, Greger M, Malaman B, Scharfe G, Kirpach C. Rheological and physico-chemical study of cement mortars with polycarboxylate-type superplasticizers. *1st International Conference – Construction Heritage in Coastal and Marine Environments. Lisbon, Portugal.* 2008.
10. Prince W, Espagne M, Aitcin P.-C. Ettringite formation : A crucial step in cement superplasticizer compatibility. *Cement and Concrete Research.* 2003, **33**:635-641.