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Investigations about the influence of fine additives on the viscosity of cement paste for self-compacting concrete

N. Diamantonis [a], I. Marinos [b], M.S. Katsiotis [a], A. Sakellariou [c], A. Papathanasiou [c], V. Kaloidas [d], M. Katsioti [a,*]

[a] School of Chemical Engineering, NTUA, 9, Heroon Polytechniou Street, 157 73 Athens, Greece
[b] Heracles General Cement Company, 49-51 Soph. Venizelou Street, 141 23 Lycovrissi, Attica, Greece
[c] Public Power Corporation/Testing Research and Standards Center, Attica, Greece
[d] Hellenic Cement Research Center Ltd., Heracles Group, 15 K. Pateli, 141 23 Lycovrissi, Attica, Greece

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ABSTRACT

In this work, the effect of fine additives (limestone, silica fume, fly ash, pozzolan, nano-silica fume) on the plastic viscosity of cement paste is being investigated. Towards this direction, twenty-four samples were designed and produced. Those pastes consisted mainly of cement (type CEM I 42.5) and specific proportions of one or two fine additives. Plastic viscosity and yield stress were measured, as well as micro-structure of selected 28-days hardened samples was studied through means of mercury porosimetry. Results showed that limestone (40%) can improve the rheological behavior of cement pastes, and the synergy of limestone (20%) and fly ash (20%) can lead to higher packing density. Cement pastes that combine those two characteristics, could serve as the base for self-compacting concrete (SCC) production.

1. Introduction

Self-compacting concrete (SCC) can be characterized as a very easily flowing concrete that has the ability to maintain its stability. It can spread quite easily and fill the forms without problems such as blocking and segregation [1–3]. The history of SCC goes back in the decade of 1990, in Japan, and since then, it has been widely used in the domain of constructions [4].

Generally, SCC consists of the same basic components as the Conventional Concrete (CC). However, due to its high content in fine materials such as limestone, fly ash, silica fume and pozzolan, the microstructural characteristics may differ [3,5]. Since the birth of SCC, a great part of research has been focused on the effect that some additives can have on the hydration, mix design and workability [3,6–10].

SCC mix demand greater cement paste content, as well as larger quantity of fine materials than the conventional concrete. SCC could be characterized as a sink for fine materials, which could lead to a great contribution to wiser and more environmentally friendly disposal [1].

The rheological properties of SCC should meet the demand for sufficient workability and no segregation, at the same time. Compared to those of CC, the rheological properties of SCC have lower values for yield stress and plastic viscosity. As an additional component of the SCC, the fine materials are powders with large specific surface, which has measurable impact on the rheological properties of fresh concrete [7,11–14].

The tools for rheological characterization of pastes are elementary and only a relatively small number of studies have been devoted in analysis, understanding and standardization of rheological behavior of such materials. Generally, it is thought that concrete's behavior is that of a Bingham fluid. Many researchers, such as Banfill and DeLarrard, have successfully used the Bingham model to simulate the behavior of SCC. According to that, there are two parameters that define the flow: the yield shear stress and the plastic viscosity [15].

Plastic viscosity is by definition different from the apparent viscosity, which can apply only on Newtonian fluids. Yield shear stress is related to the ability to spread. Plastic viscosity can be related to properties such as easiness of setting and pumping, as well as the finishing result. Moreover, the resistance to segregation can be defined as the ability of aggregates not to sink into the cement paste. This phenomenon is linked to the plastic viscosity of the cement paste and the mix design of concrete [8].

The granulometry characteristics of the solid content have an important effect on the values of yield shear stress and plastic viscosity. The objective of this study is to investigate the rheological behavior of the cement paste, aiming at the understanding and standardization of the role of grain phases on the rheological

* Corresponding author. Tel.: +30 210 7723206; fax: +30 210 7723188.
E-mail address: katsioti@central.ntua.gr (M. Katsioti).

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characteristics of the mixture, with the assumption that SCC, in its fresh condition, is a system with two phases; one solid grain phase dispersed in the fluid phase of cement paste [16,17]. Furthermore, an indirect investigation of the impact of the additives' packing density on the micro-structure of solid, hardened cement paste is conducted [18,19].

This work aims at the study of the effect that some fine materials have on the rheological behavior of the cement paste, when they act as additives. Rheological characteristics (plastic viscosity and yield shear stress) have been measured, as well as the micro-structure with mercury porosimetry.

2. Experimental

The fine materials that were used as additives are the following: earth of Milos (natural pozzolan deriving from the Greek island of Milos), fly ash, silica fume, limestone and nano-silica fume in the form of suspension (product CEM BINDER 8 as supplied by EKA). In the mixtures that were prepared, specific percentages of the contained cement were substituted by the prementioned materials. The cement was of type CEM I 42.5 and was kindly offered by "Heracles" General Cement Company in Greece. Limestone, fly ash and pozzolan that were used as additives were of Greek origin. Silica and nano-silica fume were kindly offered by "Hellenic Cement Research Center". The weight content of all samples is shown in Table 1, while in Table 2 the specific surface and weight of the raw materials are presented.

The size distribution was determined with the use of a Cilas Model 1064 laser diffractometer on a suspension of 0.1 g of sample in ethanol.

For the study of the effect of fine additives on the rheological behavior of the cement paste, mixtures of materials and cement were produced and then mixed using a w/c ratio equal to 0.6 to a final volume of 400 mL. It should be noted that the total cement mix is considered as cement. The mixtures were split to two categories, one with low concentration in additives and another with high concentration, 20% and 40% respectively. Moreover, additional mixtures were prepared by substitution of 5% admixture with silica fume. Ternary mixtures were prepared as well, containing cement and two of the additives with concentration of 20% each. Finally, in some selected mixtures, an addition of nano-silica fume was performed, in quantities of 0.1%, 0.3%, 1.0% w/w.

Table 2
Specific surface and weight of raw materials.

Raw material	Specific surface, cm^2/g	Specific weight, g/mL
Cement	3830	3.15
Silica fume	8030	2.23
Limestone	6010	2.76
Pozzolan	6050	2.36
Fly ash	6090	2.48

The mixing procedure consisted of two steps, first mixing the powder materials and then mixing them with the water. Especially for the nano-silica fume, due to its suspension nature, it was first dispersed in the water and then the rest of powder materials were added.

In total, twenty-four mixtures and one reference were prepared. The exact quantities of the materials used are shown in Table 1.

Limestone, pozzolan and fly ash underwent a grinding process in a ball mill before mixing, so as to increase their specific surface and create a more homogeneous particle size distribution. The final value of specific surface was about 6000 cm^2/g measured by Blaine method. The properties of all raw materials are mentioned in Table 2.

In terms of specific surface, it should be noted that silica fume has the greatest value of 8030 cm^2/g, while cement has the smallest one at 3830 cm^2/g.

The equipment used for the measurement of the rheological properties of the mixtures is listed under the category of cylindrical coaxial viscometers. The viscometer is manufactured by Fann Instruments and the model is "Fann Model 35 S/A Viscometer". The measurements were conducted at six velocities of 3, 6, 100, 200, 300, 600 rpm. These experiments were hosted by the Research Center of Public Power Company s.A. in Greece.

Table 1
Weight content % w/w for the cement pastes.

Mixtures code names	Cement (C)	Silica Fume (S)	Limestone (L)	Pozzolan (P)	Fly ash (FA)	Nano-silica fume (NS)[a]
20%P	80			20		
40%P	60			40		
20%FA	80				20	
40%FA	60				40	
20%L	80		20			
40%L	60		40			
15%P–5%S	80	5		15		
35%P–5%S	60	5		35		
15%FA–5%S	80	5			15	
35%FA–5%S	60	5			35	
15%L–5%S	80	5	15			
35%L–5%S	60	5	35			
20%L–20%P	60		20	20		
20%P–20%FA	60			20	20	
20%L–20%FA	60		40		20	
40%L–0.1%NS	60		40			0.1
40%L–0.3%NS	60		40			0.3
40%L–1.0%NS	60		40			1.0
20%P–20%FA–0.1%NS	60			20	20	0.1
20%P–20%FA–0.3%NS	60			20	20	0.3
20%P–20%FA–1.0%NS	60			20	20	1.0
20%L–20%FA–0.1%NS	60		20		20	0.1
20%L–20%FA–0.3%NS	60		20		20	0.3
20%L–20%FA–1.0%NS	60		20		20	1.0
100%C (reference)	100					

[a] The percentages in the table refer to w/w quantity of material that is added to the mixture.

The measurements results had to be processed according to the viscometer manufacturer's instructions [20]. This process leaded to quantitative results for plastic viscosity and yield shear stress.

Plastic viscosity depicts the resistance that the fluid shows when it flows.

The values of plastic viscosity for the cement paste were calculated using the Eq. (1):

$$PV = \theta_{600} - \theta_{300} \quad (1)$$

where PV is the Plastic Viscosity (cP), θ_{600} the reading on the viscometer at 600 rpm and θ_{300} the reading at 300 rpm.

Eq. (1) is derived from the following equation, taking into consideration the instrument's constants.

$$\eta = Kf\frac{\theta}{N}$$

where η is the Plastic Viscosity (cP), K is the overall instrument constant, f the torsion spring of the instrument, θ the Viscometer's reading and N the rate of revolution of the outer cylinder

The value of yield shear stress refers to the minimum value of shear stress that fluid needs in order to start flowing.

For the calculation of its value, YP, the reading at 300 rpm, θ_{300}, and the previously calculated plastic viscosity, PV, as it is shown in empirical Eq. (2):

$$YP = \theta_{300} - PV \quad (2)$$

where YP is the Yield Stress (mPa), PV is the Plastic Viscosity (cP) and θ_{300} the reading at 300 rpm.

Again, the previous equation comes from the equation

$$\tau = k_1 k_2 \theta$$

where τ is the Yield Stress (mPa), k_1 and k_2 are instrument's constants and θ the Viscometer's reading.

3. Results and discussion

3.1. Raw materials' granulometrical analysis

The cumulative particle size distribution for the raw materials is shown in Fig. 1, apart for nano-silica, which is suspended in water (mean grain size: 1 μm).

It can be easily observed that limestone is the finest material, with mean particle size of 7.5 μm, while on the other side fly ash has the biggest particle size of 25 μm.

3.2. Measurement of plastic viscosity and yield shear stress

The results of the calculations of viscosity and yield shear stress are presented in Figs. 2 and 3.

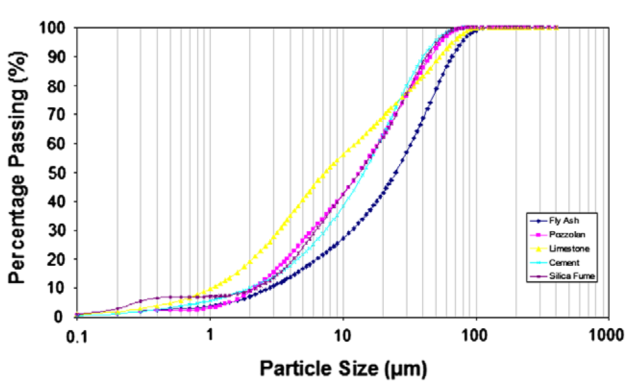

Fig. 1. Particle size distribution.

In Fig. 2, it can be seen that mixtures containing limestone have a low value of plastic viscosity (thus lower resistance to the flow). This conclusion is enhanced by the observation of the three ternary mixtures, where only the mixtures containing limestone have lower values of plastic viscosity. This behavior could stem from the better combination of particle sizes that these mixtures have, meaning that a higher packing density could lead to low flow resistance. Other researches have shown that limestone may act as filler in some occasions, which may be the case here [21].

Furthermore, plastic viscosity of these mixtures is even lower than that of the reference mixture, which is consisted only by cement and water at the predefined ratio.

It can easily be extracted from the Fig. 3 that limestone once again improves the rheological behavior of cement paste, since mixtures that contain limestone show low values of yield shear stress when compared to other mixtures, and thus they can spread more easily. Such a synthesis could be the baser for the production of SCC, since it shows very good flow ability.

Referring to the group of mixtures with high concentration of fine materials, 40%, the landscape follows similar patterns as described. The best rheological behavior is shown by the limestone based mixtures, fly ash can be found at the opposite limit, whereas pozzolan is somewhere in between, something that is illustrated in the Fig. 2.

By substituting 5% admixture with silica fume, in mixtures with low fine additives concentration (20%) notable results are observed only in pozzolan mixtures. The explanation of the latter may lie on the fact that pozzolan exhibits cementitious behavior and thus, lowering the percentage of pozzolan in the mixture, the hydration procedure is not intensified. The values approach those of limestone. On the other hand, mixtures of limestone and fly ash are not affected by silica fume.

Also, when the silica fume substitution is performed on the high concentration mixtures, it does not improve the rheological behavior. Mixtures with fly ash and pozzolan are not affected, while limestone mixtures have their plastic viscosity increased by 10%.

Silica fume has the largest specific area combined with a particle size distribution same as cement and pozzolan. That could mean the existence of pores that absorb water, thus not contributing to higher flow ability. Pozzolan on the other hand, due to its cementitious properties, it may contribute to the hydration process, leading the paste to greater adhesive properties and lower flow ability.

As a conclusion, the addition of silica fume does not act as desired, lowering the rheological behavior of the cement pastes.

The reason why limestone acts as described may lie either on chemistry or on the packing density, or on both. More specifically, from theoretical studies of filler effect, supposing that limestone does act as filler, the behavior is explained because of the retardation of hydration process that limestone causes at early stages (properties measured 3–5 min after mixing). Also, it could be caused by the better granulometrical distribution of the mixture when limestone is present. That leads to a higher packing density and subsequently to higher flow ability due to "inter-particle slip".

The addition of a small quantity of nano-silica fume (0.1%, 0.3% or 1.0%) for the production of the mixtures 40%L–$x{\cdot}x$%NS, 20%P–20%FA–$x{\cdot}x$%NS, 20%L–20%FA–$x{\cdot}x$%NS, was performed in order to examine whether this material can improve more the rheological behavior of cement paste. This does not happen, since the measured properties do not differ from the initial.

3.3. Mercury intrusion porosimetry

The porous structure of the hardened cement paste (at 28 days) was studied with the method of porosimetry with mercury penetration. The results were the cumulative and differential distribu-

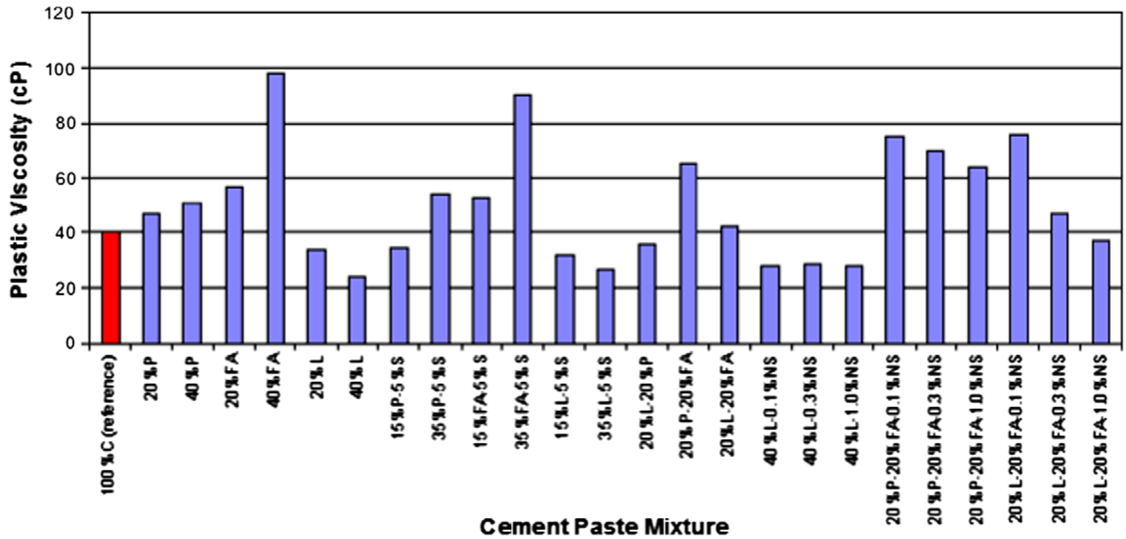

Fig. 2. Plastic viscosity for all mixtures.

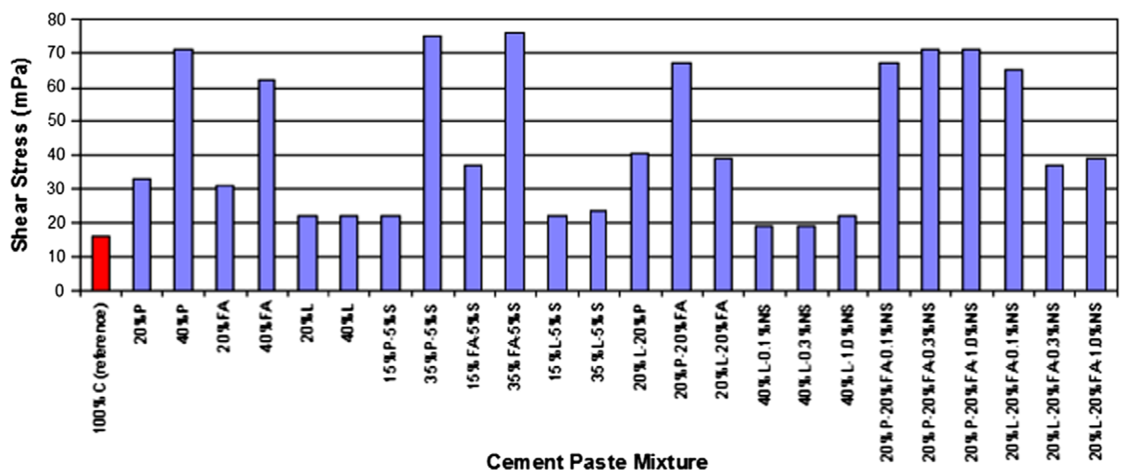

Fig. 3. Yield shear stress for all mixtures.

tion of pore volume. They have been selected the hardened cement pastes after 28 days, for the four following mixtures: 40%L, 35%L–5%S, 20%L–20%P, 20%L–20%FA, so as to compare the limestone based mixtures that showed the best rheological behavior.

The results are shown in Figs. 4 and 5:

Bulk density of the selected samples was measured and then the total porosity was calculated. The results are shown in Table 3.

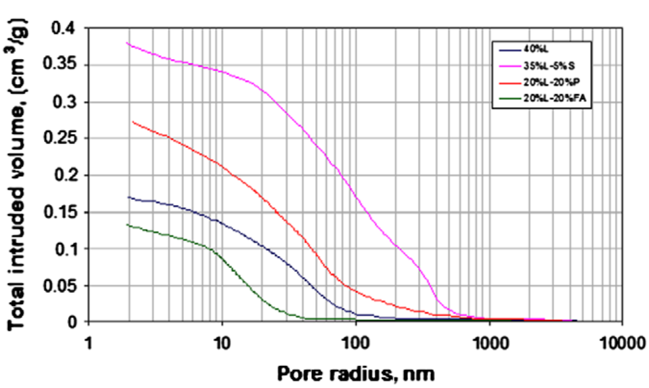

Fig. 4. Cumulative intruded volume curve.

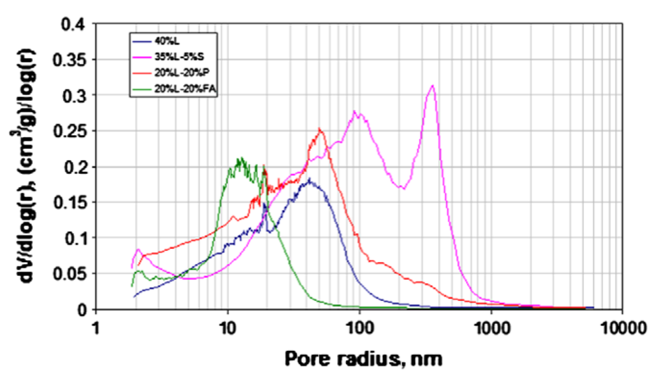

Fig. 5. Differential pore size distribution.

The lowest value is that of the mixture 20%L–20%FA, a fact that leads us to conclude that there is a synergy between limestone and fly ash that results to a denser micro-structure, due to better filling the void space among the granules. From Fig. 1, that gives the granulometry of raw materials, it can be seen that fly ash has the greatest particle size, while limestone has the smallest. Obviously, during the packing of the particles in the mixture, limestone

Table 3
Total volume and total porosity (2–10,000 nm).

	Bulk density, g/mL	Pore volume, cm^3/g	Porosity, %
40%L	1.79	0.166	29.7
35%L–5%S	1.50	0.378	56.7
20%L–20%P	1.51	0.274	41.4
20%L–20%FA	1.41	0.131	18.5

Table 4
Critical pore radii.

Mixture	Critical pore radius
40%L	41.5
35%L–5%S	358.0
20%L–20%P	50.0
20%L–20%FA	12.8

particles fill the gaps between fly ash particles [21]. In this way, it can be achieved a higher and better packing density.

Substitution of cement by 20% limestone and 20% fly ash results in smaller porosity (18.5%) and smaller critical porous radius (12.8 nm). The explanation may be found in the better packing density that is achieved with this selection of materials in the mixture.

From the differential distributions it can be extracted the critical pore radii that are shown in the Table 4. A comment that can be noted is that the combination of fly ash and limestone increases the packing density and so the critical radius is narrower.

4. Conclusions

Generally, the addition of fine materials in the cement paste has a great effect on its viscosity. Limestone can improve the viscosity, and it is proved to be the best additive at 40% content. On the other hand, silica fume and pozzolan do not seem to have the desired effects, meaning to lower the value of viscosity so as to have a more easy to flow paste.

Limestone is the best fine material that can be used as a fine additive, among the materials tested in this study. Using the limestone, a cement paste with improved rheological properties could occur, comparing to others. That paste could act as base for a concrete mixture that combined with a wisely designed size distribution of coarse grain materials could lead to a SCC mixture.

References

[1] Khayat KH, Hu C, Monty H. Stability of self-consolidating concrete, advantages, and potential applications. In: Wallevik O, NieLon I, editors. First international RILEM symposium SCC. Stockholm: RILEM Publications; 1999. p. 134–42.
[2] Skarendahl A, Petersson O, editors. Self-compacting concrete, state of the art report of RILEM Technical Committee 174-SCC, self-compacting concrete. RILEM Publications; 1999.
[3] Ye G, Liu X, De Schutter G, Poppe AM, Taerwe L. Influence of limestone powder used as filler in SCC on hydration and microstructure of cement pastes. Cem Concr Compos 2007;29:94–102.
[4] Hayakawa M, Matsuoka Y, Shindoh T. Development and application of super workable concrete. In: Bartos PJ, editor. RILEM international workshop on special concretes: workability and mixing. Paisley: RILEM Publication; 1993. p. 183–90.
[5] EFNARC, Specification and guidelines for self-compacting concrete; February, 2002.
[6] Oh SG, Noguchi T, Tomosawa F. Toward mix design for rheology of self-compacting concrete. In: International RILEM symposium on self-compacting concrete No. 1, Stockholm, SUEDE (13/09/1999); 1999. p. 361–72.
[7] Zhang Xiong, Han Jihong. The effect of ultra-fine admixture on the rheological property of cement paste. Cem Concr Res 2000;30(5):827–30.
[8] Chiara Ferraris F, Karthik Obla H, Russell Hill. The influence of mineral admixtures on the rheology of cement paste and concrete. Cem Concr Res 2001;31(2):245–55.
[9] Zhu Wenzhong, John Gibbs C. Use of different limestone and chalk powders in self-compacting concrete. Cem Concr Res 2005;35:1457–62.
[10] Felekoğlu B, Tosun K, Baradan B, Altun A, Uyulgan B. The effect of fly ash and limestone fillers on the viscosity and compressive strength of self-compacting repair mortars. Cem Concr Res 2006;36:1719–26.
[11] Geiker Mette R, Brandl Mari, Thrane Lars N, Bager Dirch H, Olafur Wallevik. The effect of measuring procedure on the apparent rheological properties of self-compacting concrete. Cem Concr Res 2002;32:1791–5.
[12] D'Aloia Schwartzentruber L, LeRoy R, Cordin J. Rheological behaviour of fresh cement pastes formulated from a Self Compacting Concrete (SCC). Cem Concr Res 2006;36:1203–13.
[13] Su N, Hsu KC, Chai HW. A simple mix design method for self-compacting concrete. Cem Concr Res 2001;31(12):1799–807.
[14] Nunes S, Figueiras H, Milheiro Oliveira P, Coutinho JS, Figueiras J. A methodology to assess robustness of SCC mixtures. Cem Concr Res 2006;36(12):2115–22.
[15] Petit Jean-Yves, Wirquin Eric, Vanhove Yannick, Khayat Kamal. Yield stress and viscosity equations for mortars and self-consolidating concrete. Cem Concr Res 2007;37:655–70.
[16] Pade Claus, Self-compacting concrete: test methods for SCC, Danish Technological Institute; December, 2005.
[17] Pade Claus, Environmental impact of self-compacting concrete, ECOserve meeting in Warsaw; 18–19 May, 2006.
[18] Mahmoodi Reza Baram, Herrmann Hans J. Self-similar space-filling packings in three dimensions; December 11, 2003.
[19] Kasthurirangan Gopalakrishnan, Naga Shashidhar. Structural characteristics of three-dimensional random packing of aggregates with wide size distribution. Int J Inform Technol 2006;3(3):201–8.
[20] FANN Instrument Company, Viscometer manual, Texas, Houston, USA; 1996.
[21] Pipilikaki P, Beazi-Katsioti M. The assessment of porosity and pore size distribution of limestone Portland cement pastes. Construct Build Mater 2009;23(5):1966–70.