Superplasticizer Polymeric Additives Used in Concrete

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This paper refers to the preparation of durable performance concrete using superplasticizer additives. The study revealed the influence of polymer additives on the nature and concentration of physical and mechanical characteristics of concrete obtained as compared with a standard concrete (without additives).

Keywords: concrete, polymeric additives, superplasticizers, lignosulfonates, ether polycarboxylates

Concrete is a composite material obtained by mixing cement mixture, aggregates and water. Besides these basic components, concrete contains additions and/or additives.

The concrete performances, depend on the quality of component materials, their proportions, the place and the exposure conditions. The quality of raw materials used in clinker manufacture, conditions of calcination, fineness and particle size of cement, the relative proportions of cement and the water amount, all influence the physicochemical behavior of cement grout. Furthermore, the type of cement, aggregates nature, water, mixing temperature, additives and the environment will determine the physical, chemical behavior and durability of concrete [1].

The superplasticizers added in small amounts, affect many properties of concrete, from the time the water comes into contact with dry ingredients of concrete to long-term behavior.

Superplasticizers advantages are high water reduction (up to 40%), increased mechanical strength, increased impermeability and increased durability.

In order to obtain high strength fluid concrete, new types of superplasticizer have been discovered and developed.

Concrete with superplasticizer has a low w/c ratio, is used in combination with silica fume to obtain concrete strength above 100 MPa, improves the surface appearance, can be placed in difficult areas, and it does not vibrate.

The high water reducing additives/superplasticizer are synthetic water-soluble organic substances that significantly reduce (up to 40%) the amount of water needed to achieve a certain consistency of concrete (of higher compression, very workable) [2].

This effect can be used in two ways:

1) to reduce the water content so as to increase the strength and reduce the permeability (increased durability);

2) as cement dispersant of the same water content to increase consistency and workability.

To obtain high-performance concretes water reducing additives (especially superplasticizers) are used. They may be of the type shown in table 1.

Reducing water	High water reducing/Superplasticizers
- lignosulfonate acids, acid salts of lignosulfonate; - hydroxylated polymers; - carboxylic acids, salts of carboxylic acids; - sulfonated melamin or naphthalene formaldehyde condensates; - polyether polycarboxylates.	- sulfonated melamin formaldehyde condensates; - sulfonated naphthalene formaldehyde condensates; - modify lignosulphonates; - polyether polycarboxylates.

Table 1
TYPES OF ADDITIVES WATER REDUCING / HIGH WATER REDUCING

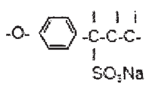
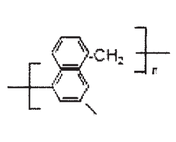
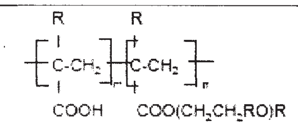
Chemical formula	Type	Year
	Modified lignin sulfonated	1930
	Sulfonated naphthalene	1970
	Polycarboxylic copolymers	2000

Table 2
TYPES OF SUPERPLASTICIZER ADDITIVES (CHEMICAL STRUCTURE)

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In the 70's the main superplasticizers were water-soluble synthetic polymers such as sulfonated melamin formaldehyde condensates, sulfonated naphthalene formaldehyde condensates, additives based on a single repeating unit (naphthalene or melamine sulfonate). The new additives studied e.g. polycarboxylates polymers [3] are based on two or more structural groups that provide greater diversity in possible molecular structures e.g changing the number of carboxyl groups per unit of polyether, polymer adsorption on the surface of cement particles can be changed significantly [4].

The molecular weight of the polyether molecules can be properly adjusted to form polymers with different characteristics to reduce the mixing water or to produce a retarding effect on initial cement hydration. Table 2 presents the chemical structures of various types of superplasticizer.

A well-known class of water reducing additives, which is a synthetic precursor of concrete superplasticizers used today, is the lignosulfonates group. Lignosulfonates are produced by lignin degradation a bisulfite extraction process of cellulose in paper industry.

Lignosulfonate molecule consists of aromatic rings containing functional groups in 3 positions, with alkoxy groups (OCH_3), ether groups (- 0 -) or polar upload substitutes or ionic groups (OH^-, COO^-, SO_3^-). Lignosulfonate is a polymer with hydrophobic and ionisable groups and/or polar functional groups.

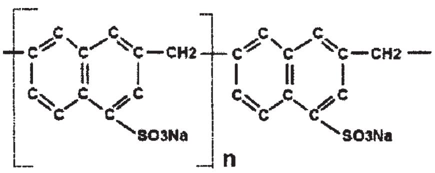
The superplasticizers can be classified into two groups:

a.the group of superplasticizer additives based on sulfonated polymers (condensed naphthalene formaldehyde sulfonate-based NFS or melamine formaldehyde condensate sulfonate-based MFS);

b.the group of superplasticizer additives based on acrylic polymers (PA), synthetic polymer carboxylates.

a. Naphthalene sulfonate-formaldehyde condensate (NSF)

Sulfonate-based superplasticizers [2] are considered to be the most important group of high water reducing additives used in all types of concrete. The best known are sulfonated poly-β-naphthalene (NFS) superplasticizers whose structure is:

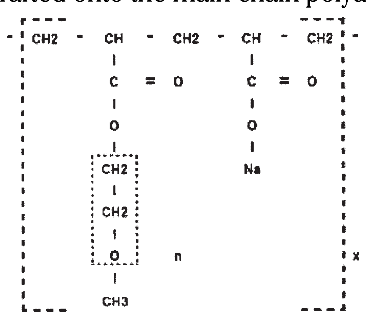


(1)

b. polycarboxylic esters

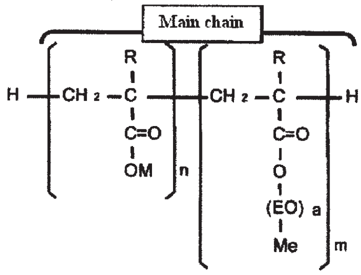
Synthetic organic polymers with carboxylic acid groups can be used as highly water reducing additives. Carboxyl groups (COOH) being a weaker acid than sulfonic groups (SO_3H), the polycarboxylates (ex. the polyacrylate) are fully ionized only in alkaline medium.

The products recently discovered such as: ethers polycarboxylates [2], are designed to work through steric stabilization resulting from the hydrophilic polyether chains which are grafted onto the main chain polyacrylic acid:



(2)

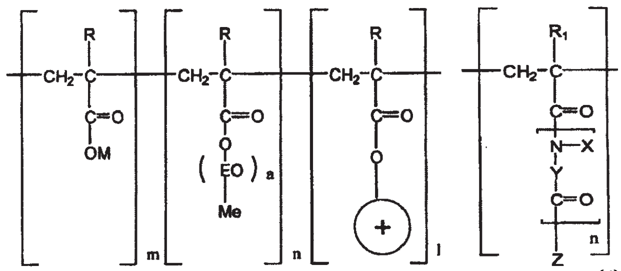
A new concept of rigidity reducing additive [5] has been developed; one type is the "multi-ion" polycarboxylic acid-based additives and the second type is polycarboxylic acid-based conventional additives. A cationic support was added to the first type and a hydrophobic one to the second type:



(3)

M = metal; EO = ethylene oxide; Me = methyl

Similar to "lego" blocks, units forming the main chain can be changed so as to alternate additives features:



(4)

By changing the functional units in the chain, the effects of additives in concrete can be modified [6]. They are mainly used for the flow control and slump loss in the ready concrete as response to the users requests.

Polycarboxylic acid-based superplasticizers can be easily synthesized from many types of polymers by changing the composition ratio of copolymers and the molecular weights and the lengths of the grafted polymer.

By using the new superplasticizer, the pressure generated by concrete pumping can be reduced by approx. 20%.

Most highly water reducing additives work in a similar way to normal water reducing additives. They dissociate in water SO_3 groups being obtained. Some are adsorbed by positive charge of cement particles, others form negative charges around the grains, reducing the interparticle attraction by electrostatic mechanism, producing a more uniform dispersion of cement grains. This reduces the amount of water needed to achieve proper consistency for cement grout.

The strong adsorption of NSF and lignosulfonate additives on the surfaces of the anhydrous or partially hydrated particles of the system can explain the influence of the admixtures upon the kinetics of the hydration process: retardation or acceleration [7, 8].

The introduction of polycarboxylate types super-plasticizers, a highly efficient water reduction class, has revolutionized the advanced concrete and mortar market.

These polycarboxylates provide significant improvements in the dispersion by electrostatic flow similar to the steric hydration of cement particles, while conventional water reducers work only by electrostatic rejection.

Recently discovered products such as ethers polycarboxylates are designed to work through steric stabilization resulting from hydrophilic polyether chains which are grafted onto the main chain (primary structure) of polyacrylic acid.

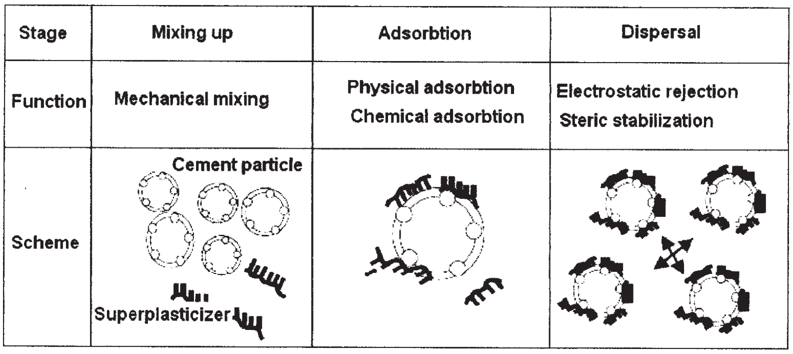


Fig. 1 - Superplasticizers mechanism

The difference between the dispersion of cement and subsequent stabilization between the types of ethers polycarboxylates and electrostatic type of rejection can be compared in figure 1 [9].

Experimental part

The basic recipe (1 m^3 concrete) cod B0 is STANDARD CONCRETE:

- cement CEM II/B-M (S-LL) 42,5 R 700 kg - slag and limestone composite cement
- aggregate: sort 0-4 mm 700 kg
  - sort 4-8 mm 292 kg
  - sort 8-16 mm 350 kg
  - sort 16-31.5 mm 603 kg
- water: 165 kg

Test were performed to different recipes with different types of superplasticizer additives with different dosages, as shown in table 3.

The tests made to characterize various types of concrete are:

- slump test (consistency determination), according SR EN 12350-2:2009;
- compressive strength, according SR EN 12390-3:2009;
- depth of water penetration under pressure, according SR EN 12390-8:2009;
- freeze-thawing resistance by measuring the variations of the resistance strength, according SR 3518:2009.

The used superplasticizers additives are: Fluiding [10] a Na-lignosulfonate, naphthalene-sulfonate based additive, Superfluid 21 [11], a modified polycarboxylates-based additive, Adi-Con SP 500 [12] a polycarboxylates ethers-based additive (table 4).

Results and discussions

The caracteristics determined are:

1. Slump, water reducing and w/c ratio

The water reducing additives of the naftalene and lignosulfonate type are commonly used in a proportion of 0.2 to 1.5% (compared to cement) producing a water reduction of 11-27%. The polycarboxylates ethers are much stronger and are used in a proportion of 0.2 to 1% of cement mass producing a reduction of water 20-40% (table 5).

At the same 27% water reduction, the BIF additive is dosed 1.5% and the BISP additive is dosed 0.2%. It is observed at the same water reduction i.e. 40% and the same 0.6% dosage, the BISF additive the slump (consistency) of 8 cm and the BISP additive has the slump 18-19 cm, being much more fluid (table 5).

For the BIF additive the w/c ratio decreases from 0.53 (0.2% dosage) to 0.42 (1.5% dosage) which leads to an increase in compressive strength without an increase in the quantity of cement.

For the BISF additive the w/c ratio decreases from 0.43 (0.2% dosage) to 0.31 (dosage 1%), and for the BISP

B0 + Fluiding (BIF)		B0 + Superfluiding 21 (BISF)		B0 + Adi-Con SP 500 (BISP)	
Dosage	Code	Dosage	Code	Dosage	Code
0.2 %	BI0.2F	0.2 %	BI0.2SF	0.2 %	BI0.2SP
0.6 %	BI0.6F	0.6 %	BI0.6SF	0.6 %	BI0.6SP
0.8 %	BI0.8F	0.8 %	BI0.8SF		
1 %	BI1F	1 %	BI1SF		
1.2 %	BI1.2F				
1.5 %	BI1.5F				

Table 3
CONCENTRATIONS OF ADDITIVES USED IN CONCRETE

Properties	Additive Type		
	Fluiding (code BIF)	Superfluid 21 (code BISF)	Adi-Con SP 500 (code BISP)
Polymer type	Na-lignosulfonate, Naphthalene-sulfonate	modified polycarboxylates	ether polycarboxylates
Appearance	Dark brown color liquid	Dark brown color liquid	Brown color liquid
Density, g/cm^3	1.16	1.11	1.08
Solid content, %	32±1.5%	39±2%	38-40
Recommended dosage, %	0.4-1	0.25-1.5	0.2-1.5
Water reduction, %	5-12	≤30	≤35

Tabel 4
SUPERPLASTICIZERS ADDITIVES PROPERTIES

Recipe/Code	Slump, [cm]	Water reducing, [%]	Ratio w/c
B0	7.5-8	-	0.6
BI0.2F	7.5-8	**11**	0.53
BI0.6F	7.5	7	0.55
BI0.8F	7	15	0.50
BI1F	7	25	0.44
BI1.2F	7.5	24	0.45
BI1.5F	7.5-8	**27**	0.42
BI0.2SF	8	**27**	0.43
BI0.6SF	8	**40**	0.35
BI0.8SF	8	37	0.37
BI1SF	7	46	0.31
BI0.2SP	7	20	0.48
BI0.6SP	18-19	**41**	0.37

Table 5
SLUMP, WATER REDUCING AND W/C RATIO

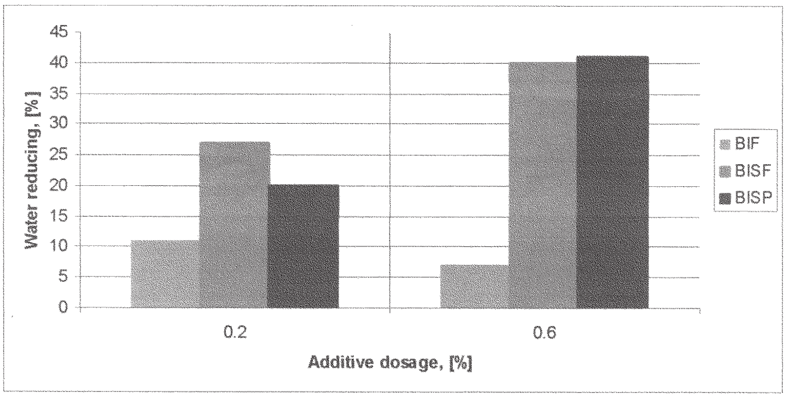


Fig. 2. Water reduction

additive decreases from 0.43 (0.2% dosage) to 0.31 (0.6% dosage).

At a 0.8 dosage of % BISF a 0.37 w/c ratio is obtained, which is equal to that of BISP additive but at a lower dosage of 0.6%.

For the same 0.2% dosage, water reduction is 11% with BIF additive (naftalene and lignosulfonate type), 27% with BISF additive (modified polycarboxylates type) and 20% with BISP additive (polycarboxylates ethers type). At 0.6% dosage, water reduction is 7% with BIF and approximately 40% with BISF and BISP additive (fig. 2).

Compressive strength

For the BIF additive the compressive strength increases, and it has a maximum at 1% dosage and then it decreases. Therefore, this is the optimal dosage. In all cases at a dosage of 0.6%, compressive strength increases significantly as compared to standard concrete, without additives B0 (table 6).

Variation of compressive strength depending on the amount of additive added in the recipe is shown in figure 3.

From a compressive C16/20 strength class for standard concrete (without additives), a higher class C30/37 is reached by the addition of 1% BIF (naphthalene-formaldehyde sulfonate-based additive), or 0.2 BISF, 0.2% BISP (polyether polycarboxylates-based additives, new generation).

A class C40/50 is obtained by the addition of 1% BISF or 0.6% BISP. About the same strength of 40 N/mm^2 is achieved with a dosage of 1% BIF, 0.6% BISF and only 0.2% BISP (fig. 4).

From standard concrete (B0), a dosage of 0.6% BISP practical leads, to a doubled compression strength.

Compressive strength after approx. 30 freeze-thaw cycles

Freeze-thaw cycles consist of exposing specimens (concrete blocks) at the temperature of 17^{0}C for 4 h and then immersing in water for 4 h at 20^0 C. After 30 cycles, the compressive strength of specimens is determined and it is compared with the compressive strength of blank specimens, immersed in water maintained throughout the duration of the performed cycles. In all cases there is a

Table 6
COMPRESSIVE STRENGTH

Recipe	Compressive strength (28 days), [N/mm^2]
B0	22.76
BI0.2F	27.68
BI0.6F	26.81
BI0.8F	30.39
BI1F	41.63
BI1.2F	35.91
BI1.5F	38.87
BI0.2SF	37.94
BI0.6SF	45.33
BI0.8SF	44.60
BI1SF	54.98
BI0.2SP	39.37
BI0.6SP	51.09

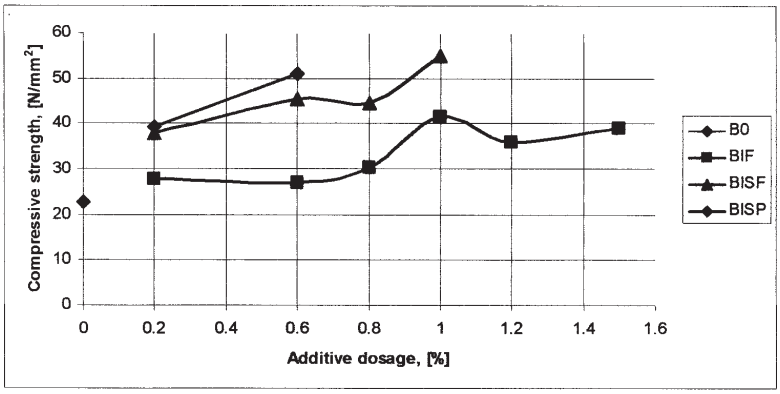


Fig. 3. Compressive strength

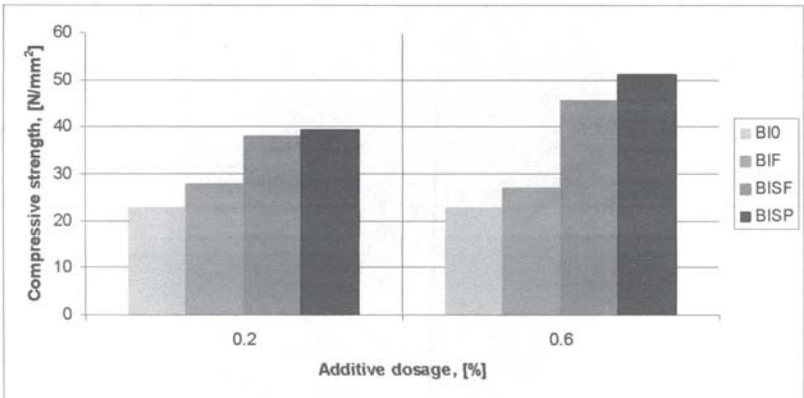


Fig. 4. Compressive strength

Table 7
FREEZE-THAWING RESISTANCE

Recipe	Compressive strength, [N/mm²]		Resistance loss, [%]
	Blank sample	Exposed sample	
B0	26.42	26.06	1.38
BI0.2F	30.57	30.28	0.95
BI0.6F	29.08	30.94	- 6.4
BI0.8F	35.35	35.00	0.99
BI1F	42.27	42.46	- 0.45
BI1.2F	39.39	37.52	4.75
BI1.5F	37.58	36.18	3.72
BI0.2SF	39.86	41.69	- 4.59
BI0.6SF	51.02	49.61	2.76
BI0.8SF	47.68	49.14	- 3.06
BI1SF	61.83	60.55	2.07
BI0.2SP	42.95	42.88	0.16
BI0.6SP	54.51	55.24	- 1.33

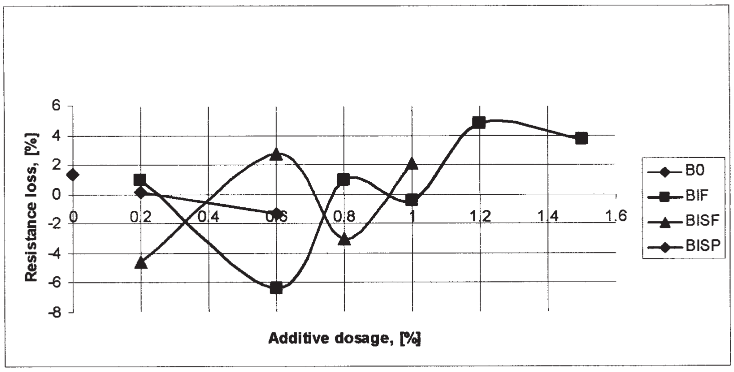


Fig. 5. Freeze-thawing resistance

small loss of strength and in some cases even an increase in compressive strength (table 7) as follows: for BIF to a dosage of 0.6%, for a dosage 0.2% and 0.8% for BISF and for BISP at a dosage of 0.6%.

Freeze-thaw resistance after approx. 30 cycles, expressed by the variation of the compressive strength depending on the quantity of additive added in the recipe, is shown in figure 5.

Depth of water penetration under pressure (8 atm)

Depth of water penetration under pressure (8 atm) decreases in all cases to B0 (10 cm) the water penetration is low according to table 8 for BI0.8SF (2 cm) and BI0.6SP (1.4 cm).

The same water penetration is achieved with a dosage of 0.8% BISF and 0.2% BISP.

Depth of water penetration under pressure depending on the amount of additive added is presented in figure 6.

Recipe	Depth of water penetration [cm]
B0	10
BI0.2F	8
BI0.6F	6
BI0.8F	5
BI1F	4.5
BI1.2F	4
BI1.5F	5
BI0.2SF	3
BI0.6SF	2.5
BI0.8SF	2
BI1SF	2
BI0.2SP	2
BI0.6SP	1.4

Table 8
DEPTH OF WATER PENETRATION

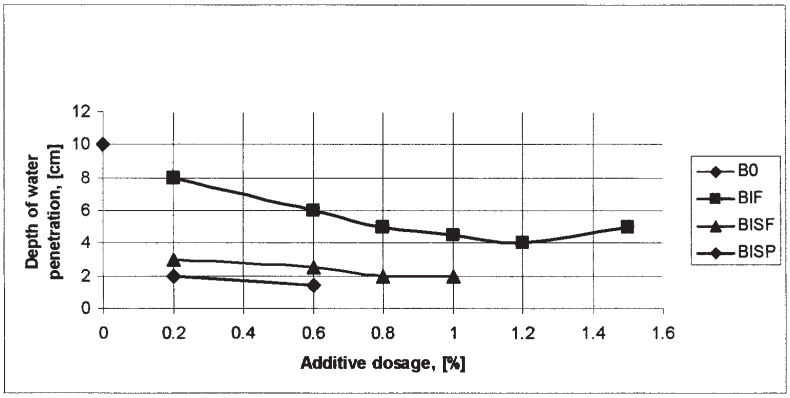


Fig. 6. Depth of water penetration under pressure (8 atm)

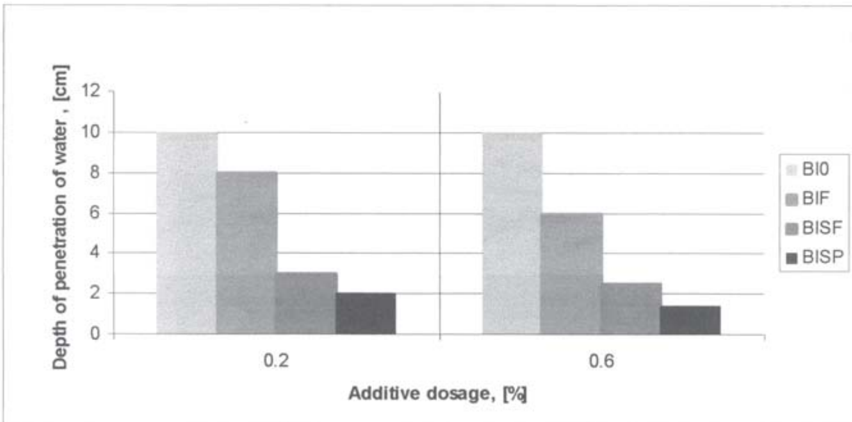


Fig. 7. Depth of water penetration under pressure (8 atm)

At the same dosage 0.2% or 0.6% the lowest water penetration is obtained when the additive BISP is used (fig. 7).

Conclusions

- water reduction (about 40%) and decrease of w/c ratio (about 0.37) correlated with the dosage of additive used is most significant when using BISP additive, which is an additive from the new generation of superplasticizer based on ether carboxylates. Compressive strength is double than that of standard concrete;

- by adding superplasticizer additives, a concrete of C16/20 class can be reach higher classes, i.e. C40/50, without changing the amount of cement;

- by assessing the results of the tests, it appears that the additive BISP is the most efficient one and this obviously leads to its use for obtaining self-compacting concretes.

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