INFLUENȚA ADITIVULUI ANTRENOR DE AER COMBINAT CU DIFERITI SUPERPLASTIFIANȚI ASUPRA REZISTENȚEI LA ÎNGHEȚ – DEZGHEȚ A MORTARELOR DE CIMENT

INFLUENCE OF THE AIR-ENTRAINING ADMIXTURE WITH DIFFERENT SUPERPLASTICIZERS ON THE FREEZE-THAW RESISTANCE OF CEMENT MORTARS

A. UĞUR OZTURK, R. TUĞRUL ERDEM*

Department of Civil Engineering, Celal Bayar University, 45140, Manisa, Turkey

Compatibility of different based superplasticizers with air-entraining admixture has been investigated. Physical and mechanical properties such as flow, setting time and compressive strength of cement mortars incorporating an air-entraining admixture (HS) with naphthalene sulfonate (SPNS) and modified polymer (SPMP) based admixtures have been determined. Also, the effects of their combinations on the freeze-thaw resistance of cement mortars have been determined. All admixtures are used with three different ratios and one of them is for overdosage effect. Results indicate that cement mortars having lowest early strength values are mortars incorporating 1.5% SPMP and 2.0% SPNS by mass of cement. The most effective series for the ultimate highest strength values were series with 0.05 % HS and 0.8 % SPMP. The freeze-thaw resistances of cement mortars were investigated for 50, 100, 150 and 200 freeze-thaw cycles. Indeed, the most effective series for freeze-thaw resistance were series with 0.05 % HS and 0.8 % SPMP.

Keywords: *Admixtures; superplasticizer; compatibility; compressive strength; freeze-thaw*

1. Introduction

Cementitious materials such as concrete or cement mortars are widely used materials in construction technology. Enhancing desired requirements expected from structural members are provided not only by using conventional concrete components such as cement, aggregate and water together, but also by using admixtures even mineral or chemical in concrete mix. Admixtures are defined as materials other than water, aggregate, cement and also fiber reinforcement used as component in concrete or cement mortar production and added to the batch before or during mixing [1, 2].

Requirement of having more durable materials and structural members during service life of a building leads site engineers to use admixtures, especially chemical ones. Chemical admixtures have some benefits on workability, set controlling, strength and durability of cementitious materials by affecting on cement paste [3].

Even chemical admixtures are not almighty; they have become more popular in concrete technology recently. Although usage of chemical admixtures is useful to improve early and ultimate properties of cementitious materials; they do not have any benefits on materials prepared with poor mix materials and unqualified workmanship during transportation, settlement and vibration [4].

Furthermore, some difficulties such as physical, biological and chemical attacks during service life of a building may be overcome by using different types of admixtures together. However; the handicap of knowledge of the reaction between these different types of admixtures and disobeying the usage limits of chemical admixtures given by the producer, lead to unexpected problems.

The types of admixtures differ so much that they must be classified into many groups according to their effectiveness on cement paste. Many such classifications have been proposed, thus it is important that each includes one admixture type having different effects on hydration process of cementitious materials. Furthermore, the knowledge of the effects occurred by using different types of admixtures together in order to improve properties and aim the desired characteristics has become a great issue. For using different types of admixtures together; the usage limits, their interaction between each other and finding out the optimum usage limits must be known. This information brings scientists or researchers to improve more durable cementitious structural members against aggressive media such as freeze and thaw.

Freeze and thaw leads an exposure in the inner structure and decrease in strength properties of cementitious materials. Freeze and thaw attack is one of the most aggressive durability problems occurred in cold regions [5-7]. Freeze-thaw problem is occurred especially when concrete is exposed to moisture and repeated cycles of freeze

* Autor corespondent/*Corresponding author,*
E-mail: tugrul.erdem@cbu.edu.tr

and thaw. As more and more concrete structures (dams, hydraulic structures and offshore structures) are being built in harsher environments, the concrete material may deteriorate rapidly after repeated cycles of freeze-thaw. Hence, demand for durable concrete has increased [8]. In this case, chemical admixtures such as air-entraining ones were developed in the late 1930s and required to cause the development of a system of microscopic air bubbles in concrete, mortar, or cement paste during mixing to prevent the damage by freeze and thaw [1].

The case of cyclic freeze-thaw damage is complex with even the water present in the finest pores of concrete present in a half bound state from the time the concrete was prepared, playing a role [9]. Several studies have been performed during last decades [10-13].

On the other hand, superplasticizers are the most used chemical admixture in production of concrete technology. Superplasticizers improve fluidity of concrete by dispersing cement particles present the cement paste [14]. Nowadays, the use of superplasticizers in concrete production is very common process [15-17]. Since there have been several studies performed [18-20].

Through the twentieth century, the number of scientific papers on cements and derived materials (mortars, concretes, and other cementitious materials) has raised in a large scale. In addition, the quality of publications has undergone exponential growth. This situation has coexisted with a period of exceptional cement industry strength. There have been many papers investigating the efficiency of admixtures with different ratios [3,20,21].

The objective of this study is to investigate the performance of chemical admixtures used together for cement mortars subjected to freeze and thaw cycles. The compatibility of air entraining admixture with two different superplasticizers (naphthalene sulfonate and modified polymer based) was investigated. Different ratios of admixtures and their combinations were used to prepare different cement mortars. The physical and mechanical properties such as initial and final setting time, flow values and compressive strengths were determined. Indeed, the performance of cement mortars after 50, 100, 150and 200 freeze-thaw cycles were obtained with respect to compressive strength development.

2. Experimental study

2.1. Materials

CEM I 42.5 Portland cement is used for the experimental studies. The chemical, physical and mechanical properties are given below in Table 1.

Air-entraining admixture compatible with ASTM C260 [21] is a liquid having active materials on its specific surface. The active materials in air-entraining admixtures are organic materials. The air-entraining admixture is obtained from SIKA and its commercial name is SIKA-AIR. The naphthalene sulfonate and modified polymer based superplasticizers are compatible with ASTM-C 494 [22] TYPE G and ASTM-C 494 TYPE A/D/G, respectively. The properties of admixtures are given in Table 2.

2.2. Methods

The aim of the usage of combinations of air-entraining admixtures with two different based superplasticizers is to focus on the compatibility of using admixtures together and their resistance against freeze-thaw cycles with respect to compressive strength loss. Setting time by using a Vicat Apparatus [23], flow values were obtained according to ASTM C1437 standard. Each mortar is prepared according to ASTM C109. For

Table 1

Chemical and physical properties of CEM I 42.5

Property	Value	Property	Value
% SiO_2	18.38	(Cl^-) amount (%)	0.01
% Al_2O_3	4.80	(SO_3) amount (%)	2.82
% Fe_2O_3	3.53	LOI (%)	3.63
% CaO	63.78	Initial setting time (min)	155
% MgO	0.84	Final setting time (min)	230
% Na_2O	0.45	Specific surface cm^2/g	3640
% K_2O	0.80	(2 day) strength N/mm^2	27.60
% SO_3	2.82	(28 day) strength N/mm^2	50.40

Table 2

Chemical composition and physical properties of admixtures

Admixture symbol	Base	Density (kg/l)	pH	Type
HS	Liquid with active materials on specific surface	0.99-1.03	5.4	ASTM-C 260
SPNS	Naphthalene sulfonate	1.17-1.21	8.5	ASTM-C 494 TYPE G
SPMP	Modified polymer	1.13-1.17	5.2	ASTM-C 494 TYPE A,D,G

compressive strength test, cement mortar cubes with 50 mm were molded. Cement mortars with a water/cement ratio of 0.485 and a sand/cement ratio of 2.75. Compressive strength developments of each cement mortar mix were determined.

Ratios of other components of cement mortars were kept constant; only admixture dosage, types and combination ratios were changed. All tests were performed in the laboratory conditions such as 20±2 ºC and 75-80% relative humidity. Compressive strength values were obtained for 2, 7 and 28 days.

Freeze and thaw resistance were determined after 50, 100, 150 and 200 cycles. All cement mortars with the age 28^{th} day were put into climatic test cabinet keeping inner temperature at -25ºC during 12 hours. Then all specimens were put into sodium chloride solutions in laboratory conditions for 12 hours.

3. Results and discussions

Setting time and flow values of each cement mortar samples are given in Table 3. Two parts; letter and numeric characters give the set name. The letter part represents the initials of admixture and the numeric characters indicate the usage ratios. For example, HS010-SPNS2.0 means a cement mortar mix incorporating with air-entraining admixture with 0.10% by cement mass and naphthalene sulfonate based superplasticizer with 2.0% by cement mass. Indeed, CM means cement mortar without any admixture.

All admixtures represented a retardation effect on the setting time of cement mortars. The most effective admixture using in nominative case, is SPMP with 1.5% ratio compared to other admixtures with the same usage ratio (1.5% by cement mass). Indeed, there is a retardation effect on setting time by using combinations of admixtures. Setting times of cement mortars prepared by combinations of admixtures have enlarged whereas the combination ratios have increased. The largest setting time period has been obtained for HS015-SPMP1.5 mix. It is obvious that the dominant admixture is the modified polymer based superplasticizer (SPMP).

Air-entraining admixture and superplasticizers are effective on workability of cement mortars. The admixtures and their combinations extended the flow values of cement mortars. Same trends observed for setting time values may be observed for flow properties. Modified polymer based admixtures are the most effective ones not only for nominative usage but also for usage with air-entraining admixture together.

Compressive strength values of cement mortars without combinations of admixtures are given in Figure 1.a-b and c respectively. Besides, compressive strength values of cement mortars incorporating with the combinations of admixtures are shown in Figure 2 and Figure 3.

Table 3

Initial/final setting times and flow values of cement mortar mixes

Set name	Initial setting time (min.)	Final setting time (min.)	Flow (mm.)
CM	153	242	116
HS005	178	280	129
HS010	185	292	132
HS015	210	315	144
SPNS1.0	205	310	154
SPNS1.5	244	345	165
SPNS2.0	275	362	172
SPMP0.8	225	328	156
SPMP1.0	248	342	166
SPMP1.5	280	369	178
HS005-SPNS1.0	185	295	142
HS005-SPNS1.5	218	320	151
HS005-SPNS2.0	245	350	163
HS010-SPNS1.0	230	334	156
HS010-SPNS1.5	255	355	168
HS010-SPNS2.0	275	370	172
HS015-SPNS1.0	240	341	162
HS015-SPNS1.5	270	364	170
HS015-SPNS2.0	278	375	176
HS005- SPMP0.8	190	300	145
HS005- SPMP1.0	225	332	153
HS005- SPMP1.5	260	365	169
HS010- SPMP0.8	235	340	159
HS010- SPMP1.0	272	368	171
HS010- SPMP1.5	285	370	177
HS015- SPMP0.8	245	350	165
HS015- SPMP1.0	275	374	173
HS015- SPMP1.5	287	405	179

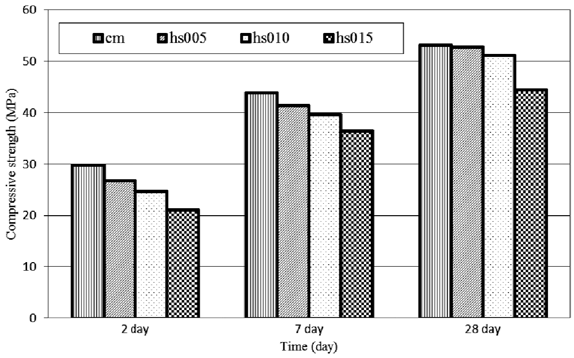

Fig. 1.a. - Compressive strength values of cement mortars incorporating with HS.

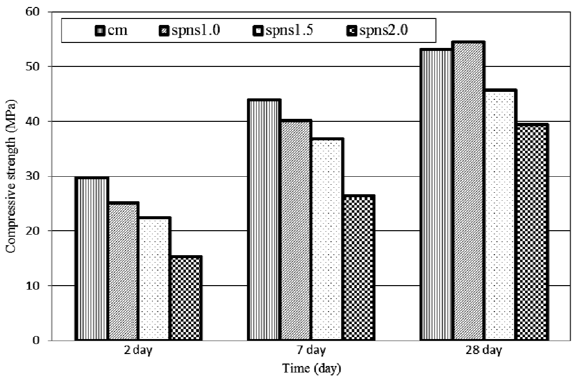

Fig. 1.b. - Compressive strength values of cement mortars incorporating with SPNS.

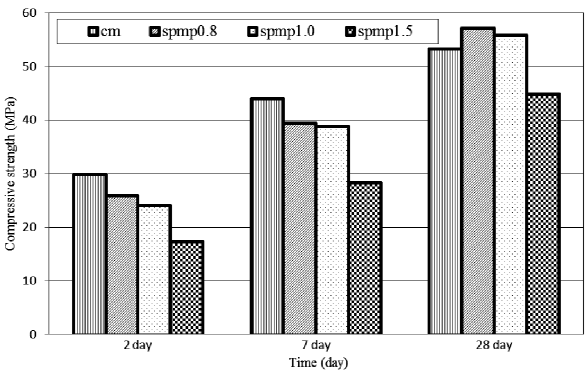

Fig. 1.c. - Compressive strength values of cement mortars incorporating with SPMP

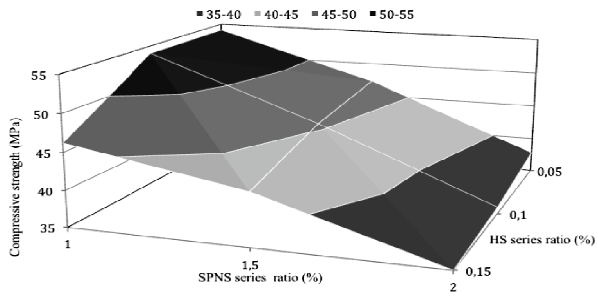

Fig. 2 - Compressive strength values of cement mortars incorporating with combination of HS and SPNS.

Although air-entraining admixture has a negative effect on compressive strength, superplasticizers improved the compressive

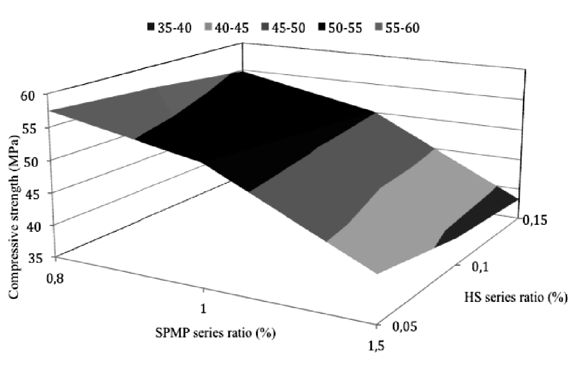

Fig. 3 - Compressive strength values of cement mortars incorporating with combination of HS and SPMP.

strength values of cement mortars at ultimate ages. At early ages, according to retardation effect on hydration of cement mortars; superplasticizers bring less compressive strength values. So, it is obvious that cement mortars with air-entraining admixtures have higher compressive strength values at early ages. On the other hand, superplasticizers formed a regular inner structure [24]. Therefore, the ultimate compressive strength values increased. At early ages such as 2 days, cement mortars incorporating with naphthalene sulfonate based admixtures have the lowest compressive strength values. The highest compressive strength values were obtained from the cement mortar samples with modified polymer based admixture with the usage ratio 0.8 % by cement mass. Indeed, higher dosages of superplasticizers affected negatively. This over dosage effects result in a lowest strength values at ultimate ages. Cement mortar samples with 1.0-1.5 % SPNS show equal or higher values compared to those with 1-1.5% SPMP. This indicates that the polymer modified based admixtures have more retarding effects on compressive strength development.

Compressive strength values of cement mortars prepared with the combination of admixtures were also determined. At early ages, HS015-SPNS2.0 series has the lowest strength values whereas the highest compressive strength values at 28 days were obtained for HS005-SPMP0.8 series. Cement mortar samples included air-entraining admixture improved their strength values by using superplasticizers together. It may be due to propagation of bubbles formed according to the presence of air-entraining agents by superplasticizers more regularly.

Freeze-thaw resistances were determined with respect to compressive strength values after 50, 100, 150 and 200 cycles. Compressive strength values after freeze–thaw cycles were represented in Figure 4 a-b-c and Figure 5 a-b. Compressive strength values of all cement mortars decreased while the numbers of freeze-thaw cycles increased.

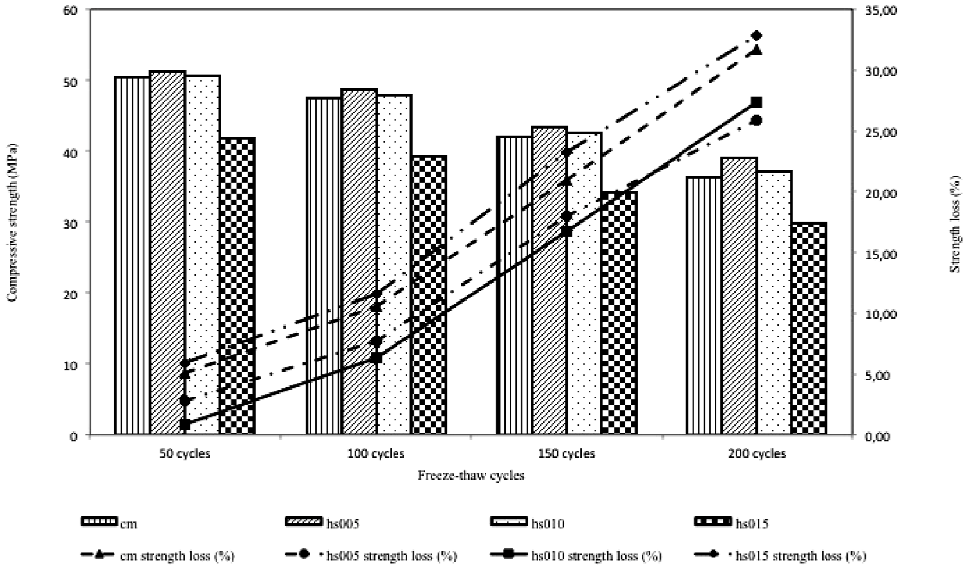

Fig. 4.a. - Compressive strength values of cement mortars incorporating with HS after freeze-thaw cycles.

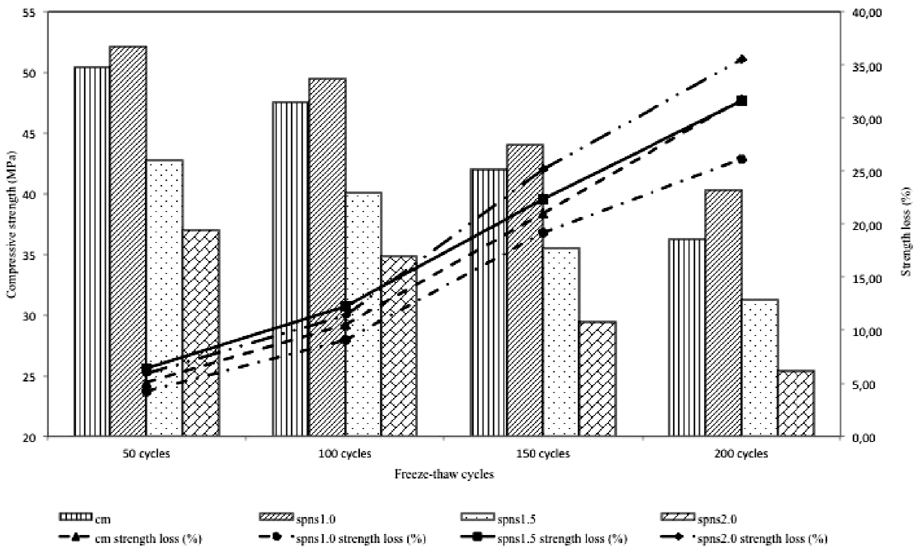

Fig. 4.b - Compressive strength values of cement mortars incorporating with SPNS after freeze-thaw cycles.

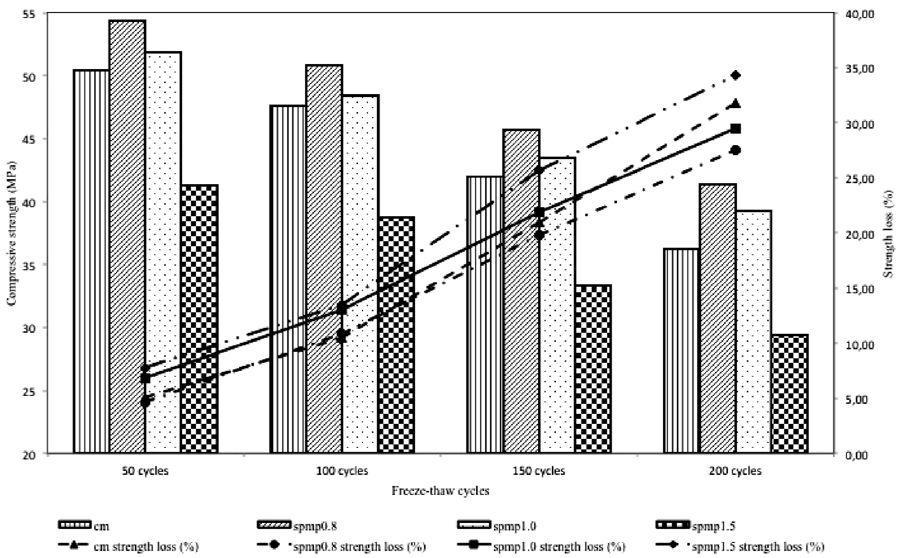

Fig. 4.c - Compressive strength values of cement mortars incorporating with SPMP after freeze-thaw cycles.

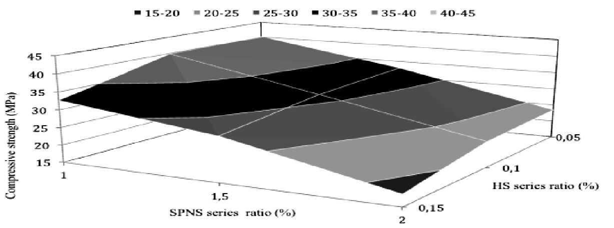

Fig. 5.a - Compressive strength values of cement mortars incorporating with combination of HS and SPNS after 200 freeze-thaw cycles.

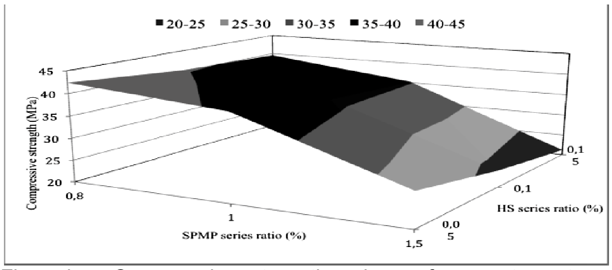

Fig. 5.b - Compressive strength values of cement mortars incorporating with combination of HS and SPMP after 200 freeze-thaw cycles.

Air-entraining admixture affected on compressive strength loss positively. On the other hand, HS015 series with the maximum usage ratio 1.5% have the lowest strength values and the highest strength loss compared to other HS series and cement mortar without an admixture. Furthermore, HS010 series have the lowest strength loss percentages. HS010 are the most effective series on freeze-thaw resistance. HS015 series and cement mortars have almost the same strength loss.

Cement mortars incorporating with 1.0% naphthalene sulfonate based admixture; have a better freeze-thaw resistance compared to cement mortars without an admixture. By the way, SPNS1.5 and SPNS2.0 have the lowest strength values. SPNS 2.0 have the highest strength loss, and even SPNS1.5 has almost the same strength loss with cement mortars without an admixture. Also, SPMP series are effective on freeze-thaw resistance on cement mortars. SPMP1.5 series have a negative effect on freeze-thaw resistance. Furthermore SPMP0.8 and SPMP1.0 have a positive effect. Indeed, SPMP0.8 series have the lowest strength loss values among SPMP series.

Indeed, freeze-thaw resistances of cement mortars incorporating with combination of admixtures were obtained. HS005-SPNS1.0 and HS005-SMPM0.8 series have the highest strength values among all cement mortars after freeze-thaw cycles. Also, highest strength loss percentages were observed for HS015-SPNS2.0 and HS015-SPMP1.5 series. Cement mortar samples with HS and 1.0% SPNS show better resistance compared to those with HS and 1.0% SPMP. The polymer modified based admixtures have more retarding effects on compressive strength development. These samples with lower compressive strength values show the highest strength loss after freeze-thaw cycles.

Cement mortar samples included air-entraining admixture improved their freeze-thaw resistance by incorporating with superplasticizers. However, the highest usage ratios of admixtures are not suitable for freeze-thaw resistance. High strength loss was obtained from such cement mortars incorporating with highest ratios. This resistance improvement may be occurred due to the highest 28-day strength performance that indicates more regular and compact inner structure having less porous structure.

4. Conclusions

In this paper, cement mortars were prepared with chemical admixture; one air-entraining and two different based superplasticizers in the first place. Some conclusions may be found out from the result of experimental study. The lowest flow values, setting time and early age strength values were measured for HS005 series. The highest ultimate strength values were obtained for HS005-SPMP0.8 series.

Freeze-thaw resistance of cement mortars incorporating an air-entraining admixture with different types of superplasticizers was investigated, indeed. All chemical admixture types have a positive effect with the lowest usage ratio. The optimum combination of chemical admixtures against freeze-thaw cycles are 0.05 % HS with 1.0 % SPNS (HS005-SPNS1.0) and 0.05 % HS with 0.8 SPMP (HS005-SPMP0.8). The highest strength losses after freeze-thaw cycles were obtained for the combination of admixtures with the highest usage ratios.

Thus, the test results must be proved for different based of air-entraining admixtures and superplasticizers. Also, different types of cements may be used in further studies for effects of combinations of admixtures in various amounts.

REFERENCES

1. xxx, ACI 116R-00, Cement and Concrete Terminology, American Concrete Institute, 2000.
2. xxx, ASTM C125, Standard Terminology Relating to Concrete and Concrete Aggregates, Annual book of ASTM standards, 2002.
3. S. Mindess, J. F. Young, et al, Concrete (Second Ed), Prentice-Hall, Inc.: 2003.
4. A. U. Ozturk, and B. Baradan, Effects of admixture type and dosage on microstructural and mechanical properties of cement mortars, KSCE Journal of Civil Engineering, 2011, **15**(7), 1237.
5. K. Bryant, and M. Bryant, Concrete durability, ACI Special Publication, 1987.
6. P. Soroushian, M. Nagi, et al, Freeze–thaw durability of lightweight carbon fiber reinforced cement composites, ACI Materials Journal, 1992, **89**(5), 491.
7. M. G. Alexander, and B. J. Magee, Durability performance of concrete containing condensed silica fume, Cement Concrete Research, 1999, **29**(6), 917.

8. S. Huai-shuai, and S. Yu-pu, Behaviour of air-entrained concrete under the compression with constant confined stress after freeze-thaw cycles, Cement and Concrete Composites, 2008, **30**(9), 854.
9. T. C. Powers, The air requirements of frost-resistant concrete, Proceedings of the Highway Research Board, Washington, 1949, p.13.
10. S. Jacobsen, E. J. Sellevold, et al, Frost durability of high strength concrete: the effect of internal cracking on ice formation, Cement and Concrete Research, 1996, **66**(6), 919.
11. A. D. Buck, Recycled concrete as a source of aggregate, ACI Materials Journal, 1977, **74**(5), 212.
12. W. Sun, Y. M. Zhang, et al, Damage and damage resistance of high strength concrete under the action of load and freeze–thaw cycles, Cement and Concrete Research, 1999, **29**(9), 1519.
13. H. S. Shang, and Y. P. Song, Experimental study of strength and deformation of plain concrete under biaxial compression after freezing and thawing cycles, Cement and Concrete Research, 2006, **36**, 1857.
14. L. Lei, and J. Plank, Synthesis, working mechanism and effectiveness of a novel cycloaliphatic superplasticizer for concrete, Cement and Concrete Research, 2012, **42**, 118.
15. V.S. Ramachandran, Superplasticizers, Progress in Cement Concrete, 1992, **1**.
16. P. C. Aitcin, C. Jolicoeur, et al, Superplasticizers: how they work and why they occasionally don't, Concrete International, 1994, **16**(5), 45.
17. E. Sakai, and M. Daimon, Mechanisms of superplastification, 1995, Materials Science of Concrete, 1995, **4**, 91.
18. I. Torresan, R. Magarotto, et al, Development of a new beta naphthalene sulfonate-based superplasticizer especially studied for precast application, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 559–582, SP-173, (1997).
19. V. M. Malhotra, Innovative applications of superplasticizers in concrete - a review, 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome, American Concrete Institute, Farmington Hills, MI, 271–314, (1997).
20. M. Collepardi, M. Corradi, et al, Influence of polymerization of sulfonated naphthalene condensate and its interaction with cement, Developments in the use of Superplasticizers, 1981, **68**, 485.
21. xxx, ASTM C260, Specification for Air-Entraining Admixtures for Concrete, Annual Book of ASTM Standards, 2002.
22. xxx, ASTM C 494-99a, Standard Specification for Chemical Admixtures for Concrete, Annual Book of ASTM Standards, 2002.
23. xxx, ASTM C 191-01a, Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle, Annual Book of ASTM standards, 2002.
24. A. U. Ozturk, B. Baradan, A comparison study of porosity and compressive strength mathematical models with image analysis, Computational Materials Science, 2008, **43**(4), 974.

****

MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

SCC16 - RILEM Self-Consolidating Concrete Conference, Washington DC, USA - From 15 May 2016 to 18 May 2016

This conference combines the RILEM Symposium on Self-Compacting Concrete and the North American Conference on Design and Use of Self-Consolidating Concrete (SCC 2016). The conference is designed to bring researchers and practitioners together to exchange the latest ideas, knowledge, and tools to build the future of concrete construction as it relates to design, construction and manufacturing of SCC.

The topics listed below are intended to spark thinking about issues that might be addressed. Other topics that address the conference theme and SCC components will also be considered.

- SCC MATERIALS (powders, nano-particles, aggregates, admixtures and microstructure
- DESIGN METHODOLOGY (mix and structural design)
- RHEOLOGY
- PRODUCTION (workability, pumping and formwork pressure)
- QUALITY CONTROL (methods, procedures and specifications)
- PROPERTY AND PERFORMANCE EVALUATION (experimentation, monitoring and modeling
- AESTHETICS AND ECONOMIC BENEFITS
- SUSTAINABILITY
- CASE STUDIES to discuss the successes and lessons learned from SCC applications

This conference will honor over 50 years of outstanding contributions of Professor Surendra Shah to the field of concrete science, including SCC research and education.

Contact: http://www.scc2016.com/

****