Pergamon

Cement and Concrete Research, Vol. 26, No. 10, pp. 1555-1566, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00138-X

SURFACE MICROSTRUCTURE AND SCALING RESISTANCE OF CONCRETE

M. Pigeon[1], C. Talbot[1], J. Marchand[1] and H. Hornain[2]
[1]Centre de Recherche Interuniversitaire sur le Béton,
Département de Génie civil, Université Laval,
Sainte-Foy, Québec, Canada, G1K 7P4
[2]Laboratoire d'Études et de Recherches sur les Matériaux
72-74, avenue Gambetta, 93170 Bagnolet, France

(Refereed)
(Received December 20, 1995; in final form August 1, 1996)

ABSTRACT

Three different types of surfaces were tested to investigate the influence of the microstructure of the surface layers on the resistance of concrete to freezing in the presence of deicer salts: troweled surfaces prepared in two different ways, and sawed surfaces. In order to perform the investigation on various types of concrete, six different mixtures were prepared using two ordinary portland cements and one fly ash. The water to binder ratio was fixed at 0,40, and the replacement level of cement by fly ash was 20% and 40% (by mass). The scanning electron microscope observations carried out clearly indicate that the first millimeters below the surface of troweled laboratory concrete specimens can have a microstructure different than that of the bulk of the concrete. In all concretes tested, an extremely porous layer (i.e. with a very high water/binder ratio) was observed at the surface. The scaling test results show that the higher porosity of the surface layers tends to markedly reduce the deicer salt scaling durability of wood troweled laboratory samples during the first cycles of freezing and thawing. The use of fly ash was found to increase the thickness and the porosity of the surface layer.

Introduction

The mechanisms related to the scaling of concrete surfaces due to freezing in the presence of deicer salts are still not perfectly clear [1-2]. Researchers have pointed out the importance of various parameters such as air entrainment [3], mixture composition [4-5], characteristics of the freezing cycles [6], and microstructure of the surface layers [6]. Although all of these factors have an influence, and although it is clear that the deicer salts are in contact with a layer of concrete that is often very different from the bulk of the material, it is not possible at the present time to identify which factors have the most importance, or predict with any degree of certainty the resistance to scaling of any type of concrete. The tests described in this paper were performed to obtain more information on the influence of the microstructure of the surface layers on the deicer salt scaling resistance of concrete.

TABLE 1
Chemical Analysis of Cements

Constituents	Cement A (%)	Cement B (%)
SiO_2	20.43	22.02
Al_2O_3	5.13	3.84
Fe_2O_3	2.66	2.84
CaO	63.19	62.78
MgO	2.22	3.70
SO_3	3.53	2.60
Na_2O	0.17	0.13
K_2O	0.85	0.43
TiO_2	0.22	0.22
P_2O_5	0.09	0.06
Free lime	0.38	0.41
L.O.I.	2.26	1.51

Research Program

To investigate the influence of the microstructure of the surface layers, it was decided to test for scaling resistance three different types of surfaces: troweled surfaces prepared in two different ways, and sawed surfaces. In order to perform this investigation on various types of concrete, six different mixtures were prepared using two Canadian type 10 cements and one fly ash. The water to binder ratio was fixed at 0,40, and the replacement level of cement by fly ash was 20% and 40% (by mass). The mixtures were designed to have a slump of 75-125 mm and 5-7% entrained air. Fly ash was used considering its possible influence on the microstructure of the surface layers. This hypothesis is supported by recent data from Johnston [7] which indicate that the scaling resistance of fly ash concrete can be particularly sensitive to the type of surface that is tested. Johnston observed a very significant difference between the scaling resistance of the top surface of a fly ash concrete specimen and that of the

TABLE 2
Physical Properties of Cements

Properties	Cement A	Cement B
Blaine specific surface (m^2/kg)	356	386
% passing 45 µm sieve	94	90

TABLE 3
Chemical Analysis of Fly Ash (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Cr_2O_3	SrO	LOI
52.7	23.5	3.8	12.5	1.2	0.3	3.6	0.5	0.9	0.11	0.1	0.01	0.1	0.8

molded bottom surface of the same specimen. The fly ash mixtures were not redesigned to take advantage of the rheological improvements fly ash normally brings, since this would have changed the selected basis of comparison, i.e. a common water/binder ratio.

Materials and Experimental Procedures

Materials. The two type 10 cements that were used are from two different plants (A and B). Their chemical and physical analyses are shown in Tables 1 and 2 respectively. The fly ash is from a Canadian source, and is referred to in this text as a class CF. It was homogenized in a closed mixer before its use. Its chemical and physical analyses are presented in Tables 3 and 4.

Granitic fine and coarse aggregates from a local source were used. Absorptivity for the fine aggregate is 0,7%, and for the coarse aggregate, 0,8%. They were used wet, and a water content test was performed in order to correct the amount of water added to the mixture. All concrete mixtures were prepared using a lignosulfonate based water-reducer and a synthetic detergent air-entraining admixture. The admixture dosages were adjusted to obtain a spacing factor of approximately 200 μm and a slump of approximately 80 mm.

Laboratory Procedures. The cementitious products, the water, and the water reducer were first introduced into the mixer, and mixed until a homogeneous paste was obtained. The fine aggregates were then added, and, finally, the coarse aggregate and the air-entraining admix-

TABLE 4

Physical Properties of Fly Ash

Specific surface (m^2/kg)	327
Density	2.09
% passing 40 μm	83.88
B.E.T. specific surface	1.20
Pozzolanicity index*	
7 days	0.76
28 days	0.89
91 days	1.08

* Measured according to the French standard (NF EN 196-1)

TABLE 5

Mixture Proportions

Mixture	Cement (kg/m^3)	Water (kg/m^3)	Fly ash (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)	Slump (mm)	Air content (%)
A	392	157	—	705	1056	95	7,2
A20	295	147	73	706	1059	90	7,2
A40	213	142	142	711	1066	85	7,4
B	395	158	—	711	1066	85	6,2
B20	299	150	75	720	1080	95	5,7
B40	216	144	144	720	1079	110	6,0

ture. Table 5 gives the information on the exact mixture compositions, together with the slump values, and the air content of the fresh concretes. All mixtures were designed to have an approximately similar paste content (28% excluding the volume of air).

After the standard mixing periods, the concrete was poured into the molds and finished using two different procedures :

Procedure 1

- filling in two layers with the use of a vibrating table;
- finishing with a wooden trowel and covering with wet burlap within 1 hour after molding;
- removal from the molds at age of 20-24 hours, and curing in lime saturated water.

Procedure 2 (ASTM C 672)

- filling in one layer and rodding one time for each 10 cm^2;
- tapping the mold to close voids and spading around the periphery with a flat trowel;
- after bleeding (2-4 hours), finishing the surface with three sawing motions (wood trowel);
- brushing of the surface and covering with wet burlap;
- removal from the molds at age of 20-24 hours, and curing in lime saturated water.

Initial setting time (ASTM C 403) was determined for all mixtures. The bleeding time as well as the amount of bleeding (ASTM C 232) were also determined.

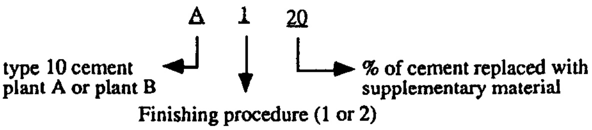

FIG. 1.
Identification code.

TABLE 6

Compressive Strength Results

Mixture	**Comp. strength (MPa)**		
	7 days	28 days	91 days
A	30.2	36.2	41.7
A20	25.0	34.7	43.7
A40	18.4	32.1	41.8
B	31.4	41.5	47.7
B20	25.2	39.5	52.7
B40	15.5	29.1	44.3

For all mixtures (Fig. 1 shows the identification code), four standard slab specimens for the scaling resistance test (2 for each finishing procedure), nine cylinders (100 mm in diameter and 200 mm in length) for compressive strength measurements at 7, 28, and 91 days, one cylinder (150 mm in diameter and 300 mm in length) cut in three for the scaling tests on sawed surfaces, one additional slab specimen for scanning electron microscope (SEM) observations, and a 100 × 100 × 200 mm prism for the air void spacing factor determination were fabricated.

The specimens for the scaling tests were cured for 14 days in lime saturated water, allowed to dry 14 days at 23°C and 50% R.H., and then resaturated for seven days with pure water prior to being subjected to 50 freezing and thawing cycles [-18°C to 23°C] with a 3% sodium chloride salt solution on the surface. They were constantly covered during the tests to prevent evaporation from the salt solution. This slightly modified version of the procedure described in ASTM C672 was selected since it is now the commonly used procedure in the province of Québec. The specimens for the SEM observations were also cured for 14 days. Samples from these specimens were then cut and placed under vacuum for 24 hours and kept in a dry a CO_2 free environment until observation. The selected 14 day curing period is relatively short for fly ash concrete, but it was nevertheless decided to use the standard curing period required by the procedure for two reasons: it is closer to normal field conditions where surface layers are generally subjected to a low degree of humidity after curing, and previous tests on fly ash concrete had indicated no significant difference between the scaling resistance of fly ash concrete cured for 14 days and cured for 28 days [8].

Test Results

Table 6 presents the results of the compressive strength tests at 7, 28 and 91 days. Considering the materials that were used and the mixture composition, the compressive strength of all mixtures is normal (Table 6). The values at 7 days are lower in the fly ash mixtures, but, at 28 days, all strength values are higher than 29 MPa. At 91 days, although the mixtures made with cement B have a higher strength, all values are higher than 41 MPa.

Table 7 gives the amount of scaling residues after 25 and 50 cycles of freezing and thawing, together with the setting time, the amount and time of bleeding, and the air void spacing factor. Bleeding is considered to be one of the parameters that can influence the porosity and

TABLE 7

Bleeding and Scaling Tests Results

Mixture	Scaling (kg/m^2)		Bleeding		Set. time	L
	25 cycles	50 cycles	(%)	(hrs)	(hrs)	(μm)
A1	0.42	0.57	1.0	2.4	6.58	216
A2	0.69	0.78				
A sawed	0.02	0.04				
A1-20	1.64	2.11	1.3	4.6	7.50	160
A2-20	1.15	1.32				
A-Sa-20	0.07	0.22				
A1-40	2.92	3.40	2.9	5.3	9.08	152
A2-40	2.81	3.46				
A-Sa-40	0.54	1.18				
B1	0.61	0.80	2.6	4.0	7.25	210
B2	0.89	1.14				
B sawed	0.02	0.03				
B1-20	1.69	2.41	2.7	5.9	8.00	178
B2-20	1.65	1.96				
B-Sa-20	—	—				
B1-40	1.52	2.66	5.1	5.5	9.08	149
B2-40	2.17	3.25				
B-Sa-40	0.74	1.12				

microstructure of the surface layers. In Table 7, it can be seen that bleeding is higher in the mixtures made with cement B, and that, for both cements, the value for the mixture containing 40% fly ash is much higher than that for the other two mixtures. The setting time is also a function of the fly ash content, but the cement was not found to have any significant influence in this respect.

The air void spacing factor is obviously also of prime importance as regards the scaling resistance. As can be seen in Table 7, all concrete mixtures have good spacing factors.

The results of the scaling tests are described in detail in Fig. 2 (troweled surfaces of all mixtures made with cement A), Fig. 3 (troweled surfaces of all mixtures made with cement B), and Fig. 4 (all sawed surfaces). These Figures show the amount of scaling residues as a function of the number of cycles.

These results clearly show that, for all troweled surface, the scaling process is very rapid during the first cycles, but much slower afterwards. For the sawed surfaces, however, the

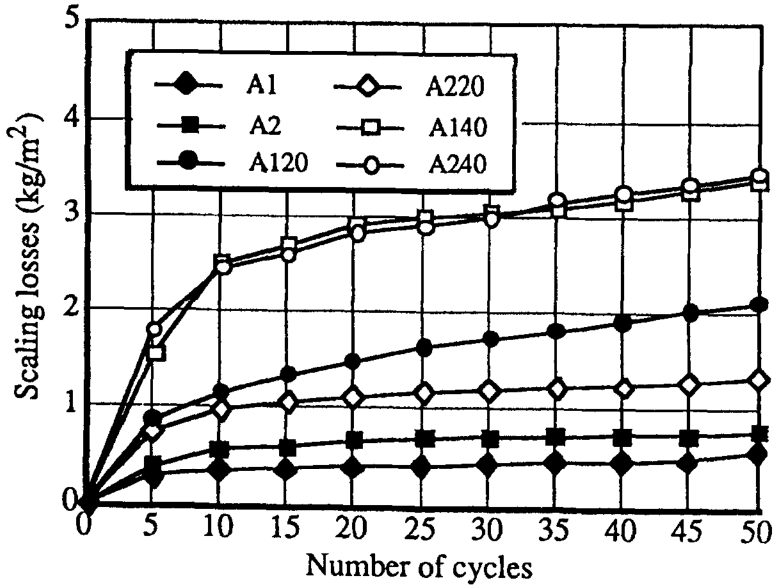

FIG. 2.
Deicer salt scaling test results for the mixtures prepared with cement A.

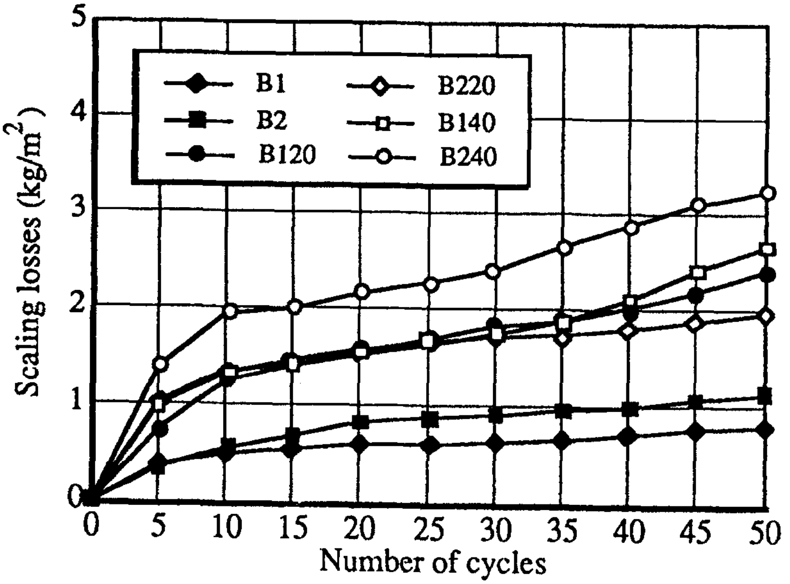

FIG. 3.
Deicer salt scaling test results for the mixtures prepared with cement B.

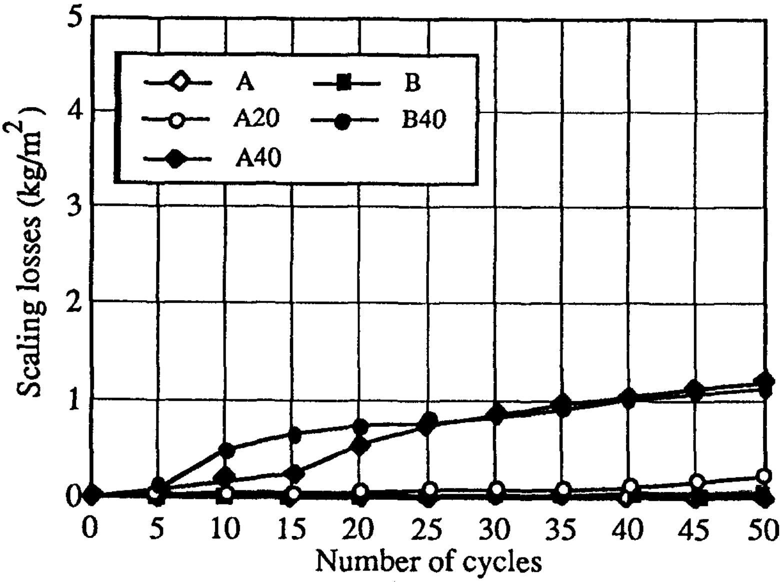

FIG. 4.
Deicer salt scaling test results for the sawed surfaces.

FIG. 5.
Microstructure of the surface layer of mixture A2 (Magnification = 2500 X).

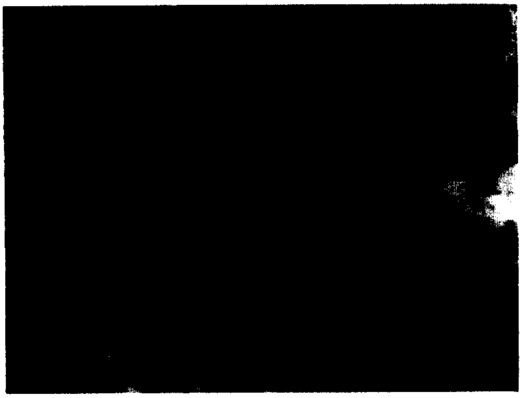

FIG. 6.
Microstructure of the core of mixture A2 (Magnification = 2500 X).

process is almost linear. Scaling increases with the fly ash content in all cases, the value for the sawed surfaces of the two mixtures containing 40% fly ash being almost equal to the usual limit of 1 kg/m^2 after 50 cycles. The results further indicate no significant influence of the finishing procedure (1 or 2), and of the cement (A or B).

Discussion

The difference between the test results for the troweled surfaces and the sawed surfaces suggests the existence of a weak zone at the concrete surface that can be easily attacked in the early stages of the scaling test. SEM observations clearly revealed that there was a zone of very high porosity under the troweled surfaces. This is illustrated in Figures 5 to 8 which show micrographs taken approximately 0,3 mm and 5 mm from the top surface for mixtures A2 and A2-40 respectively. The thickness of this very porous zone was evaluated during the SEM observations, and found to be approximately equal to 0,5 to 1 mm for A2, and more than 2 mm for A2-40. These thickness values can be clearly put in relation with the amount

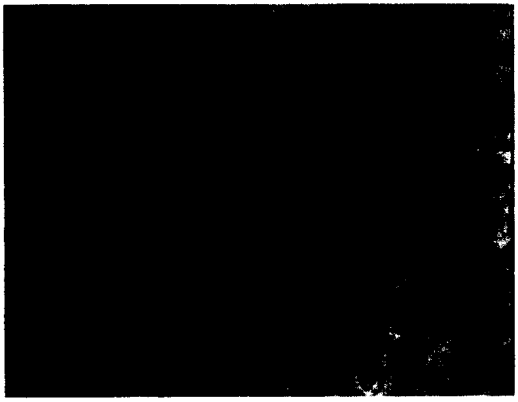

FIG. 7.
Microstructure of the surface layer of mixture A2-40 (Magnification = 2500 X).

FIG. 8.
Microstructure of the core of mixture A2-40 (Magnification = 2500 X).

of scaling residues after the first 10 cycles of the test: 0,5 kg/m^2 for A2, and 2,5 kg/m^2 for A2-40.

It is not possible, at the present time, to explain precisely the influence of bleeding on the formation of the porous layer at the concrete surface, nor the influence of fly ash on this phenomenon. But even if no direct relationship between bleeding and the thickness of the porous layer at the surface can be established, it is clear from the results in Table 6 that the amount of bleeding and the length of the bleeding period generally increased with the amount of fly ash in the mixture, that the scaling residues in the first 10 cycles also increased with the amount of fly ash, and that this can be related to the thickness of the porous layer as observed under the SEM. Fly ash can, in certain cases reduce bleeding, but this is not common [9], and bleeding may last longer in fly ash mixtures in relation to the setting time. A small difference can be noted between the test results for the mixtures made with cement A and cement B. Slightly better results were generally obtained with cement A. This can also be related to bleeding (and setting time). However, it should be emphasized that all the mixtures tested in this series were prepared at a constant paste content and W/B ratio. In that respect, as previously mentioned, no advantage of the fly ash slump-enhancing effect has been taken.

In contrast with the results for the troweled surfaces, that for the sawed surfaces (even taking into account the fact that sawing exposes aggregate as well as paste) are very low, except those for the mixtures containing 40% fly ash, which are nevertheless, as previously mentioned, approximately equal to the usual limit of 1 kg/m^2 defined in the Swedish standard [10]. The results in Fig. 4 indicate that, disregarding the influence that fly ash can have on the formation of the porous zone close to the surface, the salt scaling resistance of concrete containing 20% fly ash can be very good, and that of concrete containing 40% almost satisfactory.

After the first 10 cycles, the scaling rate for the 40% fly ash mixtures is approximately 0,02 kg/m^2 per cycle both for the sawed surfaces and for the troweled surfaces. Considering the slower reaction rate of the fly ash, the 40% fly ash mixtures after 14 days of curing could be considered to have a total porosity similar to that of a normal 0,66 water/cement ratio mixture. A scaling rate of 0,02 kg/m^2 per cycle is relatively low, especially for a high porosity mixture. It has been established that, besides the spacing factor, the amount of ice formed has a significant influence on the concrete scaling resistance [11, 12]. The volume of ice formed between 0°C and -20°C (i.e. for the temperature range of the scaling test) is lower in pastes with a finer pore structure [13, 14]. According to the scaling test results of this series, it appears that, despite its slow reaction rate, fly ash had a beneficial influence on the concrete pore structure. This is in good agreement with the results of a previous series of tests where this fly ash had been found to significantly refine the pore structure of mortars after a 28-day curing period [18].

Procedure 1, because of the use of the vibrating table, was expected to increase the thickness and porosity of the surface layer. The test results, however, do not indicate any significant effect of the finishing procedure. This again shows that an understanding of the relationship between the bleeding characteristics, the finishing procedures, and the conditions at the surface (temperature, wind velocity, and relative humidity) must be developed before the deterioration due to scaling in the field is to be systematically prevented.

Conclusion

The SEM observations carried out in this project have clearly indicated that the first millimeters below the surface of troweled laboratory samples can have a microstructure different than that of the bulk of the concrete. In all cases, an extremely porous layer (i.e. with a very high water/binder ratio) was observed at the surface. The test results also indicate that the higher porosity of the surface layers tends to markedly reduce the deicer salt scaling durability of wood troweled laboratory samples during the first freezing and thawing cycles.

The tests performed on the sawed surfaces indicate that most of the scaling deterioration observed on the troweled surfaces can be attributed to the formation of the porous layer at the surface of the concrete. Although a porous layer was observed in all concretes tested, the addition of fly ash was found to increase the thickness and the porosity of the surface layer. This effect is probably related to the fact that the fly ash used in this series of tests was found to increase the bleeding of concrete.

Research is required to understand the mechanisms of the formation of this layer, particularly since it could be influenced very significantly by the conditions existing during bleeding (particularly the rate of evaporation from the surface, which can be very different in the laboratory and in the field).

Although it is clearly possible to obtain good engineering properties with concrete containing fly ash, numerous laboratory studies have indicated that the incorporation of these supplementary cementing materials is generally harmful to the scaling resistance of concrete [15-17]. Some of these laboratory test results are in apparent contradiction with field reports where fly ash concretes are often found to have a satisfactory salt scaling durability under natural exposure conditions. The very different results obtained from the troweled surfaces and the sawed surfaces could perhaps help to explain this apparent paradox, and this also warrants further investigation.

References

1. Marchand, J., Sellevold, E.J., Pigeon, M. (1994), ACI Special Publication SP-145, Edited by V.M. Malhotra, pp. 1-46.
2. Rösli, A., Harnik, A.B. (1980), in Durability of building materials and components, Edited by P.J. Sereda and G.G. Litvan, ASTM STP 691, pp. 464-473.
3. Pigeon, M. (1989), Materials and structures/Matériaux et Constructions, Vol. 22, N° 127, pp.3-14.

4. Fagerlund, G. (1986), International seminar on "Some aspects of admixtures and industrial by-products on the durability of concrete", Göteburg, Sweden, 33 p.
5. Sarkar (1990), Cement Concrete Research, Vol. 20, N° 3, pp. 398-406.
6. Marchand, J. (1993), Ph.D. Thesis, École Nationale des Ponts et Chaussées, Paris, France, 326 p., (in French).
7. Johnston, C.D. (1994), ACI Special Publication SP-145, Edited by V.M. Malhotra, pp. 85-106.
8. Talbot, C., Marchand, J., Pigeon, M., (1996), 8th International Conference on the Duranbility of BuildingMaterials and Components, Stockholm.
9. Berry, E.E., Malhotra, V.M. (1986), Mineral Sciences Laboratories, CANMET, SP 85-3, 153 p.
10. SIS (1992), Concrete testing-Hardened concrete-Frost resistance, Standardiserings-kommissionen i Sverige, Swedish Standard SS 13 72 44.
11. Sellevold, E.J., Farstad, T. (1991), Nordic Concrete Research, Publication N° 10, pp. 121-138.
12. Hammer, T.A., Sellevold, E.J. (1990), ACI Special Publication SP - 121, Edited by W. Hester, pp. 457 - 489.
13. Powers, T.C., Brownyard, T.L. (1946), Journal of American Concrete Institute, Vol. 18, N° 8, pp. 934-969.
14. Zech, B., Setzer, M.J. (1990), Materials and Structures/Matériaux et Constructions, Vol. 22, pp. 125-132.
15. Bilodeau, A., Malhotra, V.M. (1992), ACI Special Publication SP-132, Edited by V.M. Malhotra, pp. 319-349.
16. Klieger, P., Gebler, S.H. (1987), ACI Special Publication SP-100, Edited by J.Scanlon, pp. 1043-1069.
17. Bilodeau, A., Carette, G.G., Malhotra, V.M., Langley, W.S. (1991), ACI Special Publication SP-126, Edited by V.M. Malhotra, pp. 201-228.
18. Talbot, C., Pigeon, M., Marchand, J. (1995) ACI Special Publication SP-153, Edited by V.M. Malhotra, pp. 125-152.