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SEM OBSERVATIONS OF THE MICROSTRUCTURE OF FROST DETERIORATED AND SELF-HEALED CONCRETES

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ABSTRACT

The microcracking and self healing mechanisms of concrete exposed to rapid freezing and thawing in water and subsequently kept in water have been investigated by Scanning Electron Microscopy (SEM). Non air entrained concretes of water/binder ratio 0.40 with 0 and 5 % silica fume were studied. Damage was measured as loss in resonance frequency and compressive strength. After frost exposure, concrete beams were stored three months in water. During this time resonance frequency largely recovered, whereas compressive strength showed smaller recovery. On Secondary Electron Images (SEI) of fractured surfaces hydration products mainly of the C-S-H type were seen traversing cracks at several locations after self healing, but not directly after freeze/thaw. Back Scattered Electron Images (BSEI) showed that the cracks due to freeze/thaw testing were of 1 - 10 μm width. The cracks traversed the paste and followed the interfaces of most larger aggregate particles. On BSEI self healing was seen on 300 - 1000 X magnification as partly closing of several cracks smaller than 5 μm. This was most clearly seen by switching between SEI and BSEI modes. In BSEI-mode the re-hydration products appeared less dense and the cracks appeared wider than in the SEI-mode.

Introduction

Since the pioneer work of Powers and Helmuth (1, 2) the frost deterioration of concrete has been the subject of a great deal of research. Although the deterioration mechanisms are still not today fully understood, most of the works done on the subject have clearly indicated that frost action is mainly physical in nature. In most cases, the degradation of concrete by freezing and thawing cycles is characterized by the gradual formation of microcracks. Evidence of minor chemical alterations due to the freeze thaw process has been reported. Several researchers (3-7) for instance, observed ettringite in cracks and calcium hydroxide crystals in air voids. It was hypothesized (4) that these hydration products had been leached and recrystalized during the freezing and thawing cycles.

Earlier studies (8-11) have shown that mechanical strength of cracked concrete can recover to a rather large extent, depending on concrete composition, age at test, degree of loading and storage conditions (moisture, time, temperature etc.). This recovery was attributed to a certain self healing process. In a recent study, Abdel-Jawad and Haddad (11) studied the self healing of load induced cracks, and observed that pulse velocity indicated a too high recovery compared to what was measured by compressive strength. Observations of self healing- or re-hydration products in concrete by SEM were made by Vernet (3) after freeze/thaw and More et al (12) after mechanical loading. However, none of these authors discussed the composition of the solid deposits observed to any great detail. McHenry and Brewer (14) pointed to the importance of self-healing in concrete freeze/thaw testing.

In a recent study (13), the self healing of frost deteriorated/cracked concrete beams was observed by coincidence. Due to problems with the freeze/thaw equipment, partly deteriorated beams were left frozen for some time. When the freeze/thaw test was started again, it was noted that the beams had regained some of the loss in resonance frequency. A more systematic investigation on the self-healing of concrete after frost deterioration has since been undertaken (15). The effect of frost and self healing on microstructure has been investigated by test methods such as low temperature calorimetry and Mercury Intrusion Porosimetry (MIP). The MIP-investigations have been published (16). In this paper the effect of freezing and thawing in water, and self-healing by storage in water were investigated by SEM.

Research significance

The objective of this research were to observe the microstructure of frost deteriorated and self healed concretes. It was hoped that microstructural observations could improve the understanding of the mechanisms of frost deterioration. The study of the self-healing mechanisms could also help to understand the relationship between field performance and laboratory testing. Cracks developed in field might take longer time to develop into complete cracking or scaling, compared to in a laboratory repeated freeze/thaw test where less time is given for healing. Further, self healing might be of significance for problems such as chloride ingress and mass transfer in nuclear waste containers.

Concretes

Two concretes with water/binder ratio of 0.40 were investigated. One OPC and one with 5 % silica fume. Norwegian Ordinary Portland Cement (Norcem P30), silica fume (Ila-Lilleby) and 0 - 16 mm granite aggregate (Årdal) were used. A melamine based superplasticizer was used in the preparation of both mixtures. The concretes were mixed in a horizontal counter current mixer in 50 l batches, and specimens moulded in steel moulds in two layers. Table 1 shows composition of cement and silica fume and table 2 concrete mixtures.

TABLE 1: Composition of Cement and Silica Fume (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	L.O.I.	Spes. surface
OPC	20.9	4.6	3.5	63.4	1.8	3.1	0.9	0.4	1.0	358 m^2/kg (Blaine)
SF	91.2	0.3	2.8		1.5	0.5	0.7	0.4	1.7	15-20 m^2/g (BET)

TABLE 2: Concrete Mixtures

Mix	w/c+s	s/c+s	Cement kg/m^3	Aggr. kg/m^3	SP kg/m^3	Slump cm	Air 1) vol-%	f_{c28} 2) MPa	f_{cstart} 2, 3) MPa
040-00	0.40	0	432	1799	4.92	20	1.6	69	74
040-05	0.40	0.05	409	1782	6.46	19	2.0	79	83

1) Fresh concrete 2) Moulded 10 cm cubes 3) 2 1/2 months water curing

Freeze/thaw, healing and sampling

The concretes were water cured for two and a half months, then exposed to rapid freeze/thaw in water (ASTM C666 procedure A, five cycles per day within the specified limits), and subsequently kept immersed in water at 20 °C for three months. Deterioration and healing was characterized by resonance frequency and compressive strength of 10 cm cubes sawn from the freeze/thaw exposed beams. Table 3 gives the conditions of the concretes at sampling for SEM-investigations.

As can be seen in table 3, rapid freeze/thaw resulted in severe cracking of the two non-air entrained concretes which had durability factors of 11 and 10. After immersion in water for three months of cracked beams, the relative dynamic modulus regained to 0.72 - 0.97 of the undamaged values. The compressive strength measurements after self healing showed that the increase in compressive strength was low: 4 - 5 % after an initial loss of 21 - 28 % due to frost deterioration.

Before and after freeze/thaw testing and after immersion in water for three months, slices of 10 by 10 by 2 cm were wet sawn from the centre of the beams and immersed in alcohol (ethanol) for a week. 2 cm broad pieces traversing the centre of these 10 by 10 by 2 cm slices were wet sawn. For all 6 variables, one 2 cm broad section was made. Slits were sawn for breaking off the pieces for SEM inspections. The SEM-sections were prepared by gold coating under vacuum. Polished sections for BSEI were prepared by 24 hours drying at 60 °C followed by ca 1 hour vacuum pumping, introduction of epoxy resin, hardening of epoxy and then polishing by diamond powder in alcohol. After polishing, the specimens were cleaned in an ultrasonic bath for about 30 seconds. The areas observed were about 20 by 20 mm.

TABLE 3: Condition of Concretes at Sampling for SEM-investigations

Concrete	f_c 1) (Mpa)	E_{rel} 2)	DF 3)	Condition
040-00 sound	62.4	1.00		Virgin, cured in water for 2
040-05 sound	73.7	1.00		1/2 months
040-00 deteriorated	49.0	0.51	11	Freeze/thaw deteriorated in
040-05 deteriorated	52.6	0.23	10	ASTM C666 proc.A
040-00 self healed	51.3	0.97		Self healed, stored in water at
040-05 self healed	55.9	0.72		20 °C for 3 months

1) 10 cm cubes sawn from beams 2) E_{rel} = Relative dynamic modulus = $(f_{stop}/f_{start})^2$ where f: resonance frequency 3) Durability Factor according to ASTM C666

Scanning Electron Microscopy

A Jeol JSM 840-A scanning electron microscope equipped with a NORAN EDXA-detector and Tracor Northern back scattered electron image analysis system was used. Studies of the fractured surfaces by secondary electron images were performed at 1000, 5000 and 10000 X, whereas studies of polished sections by BSEI were performed at 50, 300 and 1000 X. BSEI inspections were performed by scanning at 50 X in a grid pattern of about 0.5 mm and studying the back scattered electron images at each stop. Observations at 300 and 1000 X were performed at each stop by moving around and following paste/aggregate bond zones and cracks. Some investigations were performed at larger magnifications (crack widths and EDXA-spectra, the X-ray beam covering an area of about 200 by 300 nm).

The study of cracks in concrete is not an easy task because of the possible introduction of cracks and structural changes at sampling, preparation and observation. The artefacts introduced during sampling, preparation and observation in SEM have been discussed by Diamond (17) in a recent review on the development of SEM-techniques for Hardened Cement Paste (HCP) and concrete. Also Hornain (18) and Ollivier (19) have discussed this topic. Fractured surfaces will most probably follow weaker zones and therefore not give a good representation of the bulk microstructure. The preparation using drying of various kinds or/and vacuum, and the vacuum during observation may introduce shrinkage cracks and alter parts of the microstructures. Further, the small size of the areas observed in SEM might make them less representative. The information obtained from SEM-inspections of concrete should be evaluated bearing such factors in mind.

Back Scattered Electron Images (BSEI)

Back Scattered Electron Images (BSEI) give important information alone, or supplementary information to Secondary Electron Images (SEI) and other techniques such as EDXA. The grey scale level of the image is a function of the mean atomic number of the phases studied. Black areas represent pores whereas white areas represent the densest phases (mostly unreacted cement grains). Scrivener and Pratt (20) developed and used BSEI for studies of HCP and concrete microstructures. Quantification of the microstructural components in HCP were made using image analysis to calculate area fractions of different grey levels on the BSEI. Kjellsen et al (21, 22) used BSEI/image analysis for studies of development of concrete microstructures at different curing temperatures. The usefulness of grey level histograms will be influenced and limited by both the type of sample and preparation. If the samples are concretes with large aggregate size and varying amount of cement paste and voids, this will completely overshadow variations in the paste. Preparation/polishing operations might also affect the comparison of images if they introduce variations in surface defects. However, the images can still give valuable qualitative information about cracks, bond zones between aggregate and paste, reaction rims around unreacted cement grains, faults and pores of various sizes and origins, and solid deposits in cracks and pores.

Observations

SEI on fractured surfaces:

The sound concretes (before freeze/thaw) were characterized by a rather dense microstructure. Rather few cracks were observed, and no evidence of alterations or recrystallization was seen.

The number of cracks seen in the frost deteriorated concretes was much higher than in the sound concretes. In the cracks, no hydration products other than those part of the original cement paste, could be detected. Apparently the short time before immersion in alcohol had prevented further hydration.

On the specimens taken from the self healed concretes, hydration products could be seen on several locations traversing the cracks. These products were mainly needle or plate shaped and were locally bridging the cracks. They were sometimes thinner in the middle and thicker at each side of the crack, and were most easily detected by following along cracks. Scanning across the specimens in grid revealed less information. At some points these hydration products appeared dense, and formed intertwined, closely knit bridges across the cracks. The majority of the cracks seen on the surfaces were less filled and the features of the cracks more clearly visible. There was a clear tendency that more re-hydration products could be seen in the cracks of the OPC-concrete than in the concrete with 5 % SF. Figures 1 and 2 show photos taken at 1000, 5000 and 10000 X in self healed cracks of the 040-00 concrete. EDXA-spectra showed mostly C-S-H-type composition, but also ettringite and calcium hydroxide types were observed. These spectra are, of course, mainly indicative of the composition. The EDXA-spectra in figure 3 show C-S-H type composition at the side of the crack, and in the rehydration products in the crack of figure 1.

BSEI before frost exposure:
Observing the sound specimens of both concretes, rather few cracks could be seen at 50 X magnification. Bond zones between paste and aggregate, in general, seemed good. The cracks that could be seen on this magnification traversed both paste, aggregate particles and bond zones. The crack widths were in the order of 1 - 10 µm, as judged on larger magnifications. Although rather small, they will be referred to here as large cracks. These large cracks were in most cases filled with resin. Cracks of less than 0.5 µm width on the interface between resin in crack and concrete could frequently be seen. This was best seen on SEI (3000 X), where the resin was seen clearly. These cracks may be due to shrinkage after the impregnation process. In addition to the large cracks, lots of small discontinuous cracks of around 0.5 µm width not filled with resin, could be seen in the cement paste at 300 and especially 1000 X. The distribution of these small cracks was uneven. In some regions, they appeared with a quite dense pattern and of somewhat varying width and length, though generally with width around 0.5 µm and much shorter than the larger cracks, whereas in other regions they were less numerous. No difference in the amount or appearance of cracks between the two concretes could be distinguished. These kind of cracks were not seen on fluorescent impregnated polished sections by optical microscopy in (15). The bond zones between paste and aggregate were in general dense with only a small crack or opening in the magnitude of 0.5 - 1 µm (4000 X). The edges of the cracks were sharp and clearly seen. The characteristics of the small cracks and the transition zones between paste and aggregate were studied by switching between SEI and BSEI (2000 - 4000 X). A shadow effect appeared on BSEI making the small cracks look a little wider, or their edges "softer", than as judged by SEI. On SEI the paste at the edges of the cracks looked brighter than the adjacent paste.

On the edge of the unreacted cement grains a small, more porous (darker) rim could often be seen. In some cases these types of "reaction rims" could be seen inside the unreacted cement grains. Pores in the size 1 - 10 µm could frequently be observed throughout all parts of the paste. They resembled what has been referred to as Hadley grains in other investigations of high strength concretes with lower water/binder ratio (23). No quantitative differences between the concrete with and without 5 % silica fume could be distinguished from the two sections. Larger air voids and a few defects could also be seen. The defects were differentiated from the voids by their predominantly angular shapes. They occurred sometimes in parts of aggregate particles and

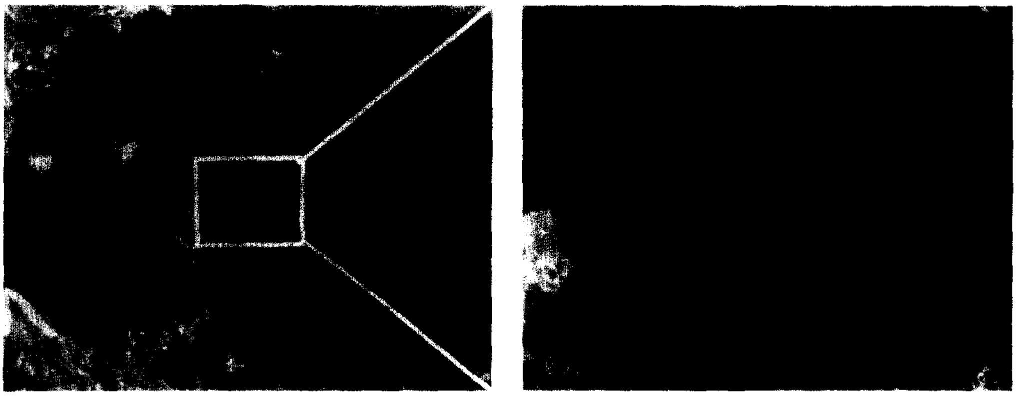

FIG. 1 (a) and (b)
SEI (1000 and 5000 X) 040-00 rehydration in crack, C-S-H type

FIG.2
SEI (10000 X) 040-00 rehydration in crack, C-S-H type

sometimes in the paste. Their sizes were in general smaller than the air voids. These angular defects result from the polishing/preparation operations. The few spherical air voids that could be seen (both concretes were non-air entrained), had maximum size of about 200 μm. Figure 4 (a) shows a BSEI of 040-05 before frost (50 X), with a void.

BSEI on frost deteriorated concretes:
At 50 X, a number of large cracks were seen in both concretes. They were clearly more numerous than in the sound specimens. The cracks passed through paste and followed the boundaries of most larger aggregate particles. At larger magnifications the crack widths were seen to be 1 - 10 μm, i.e. the same size as the few large cracks seen before frost exposure. These cracks were the same as the ones observed by optical microscopy in (24). Very few of the larger cracks were not filled with resin. At higher magnifications, the same type of small cracks, as in the sound specimens, could be seen in the paste, and between resin and concrete in large cracks. The same

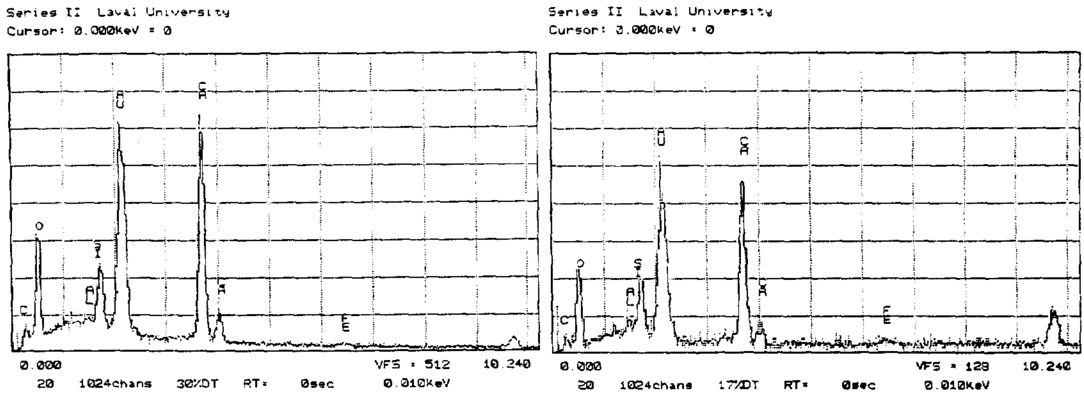

FIG.3 (a) and (b)
EDXA-spectra taken at the side of the crack and in the crack of FIG.1 (both C-S-H type)

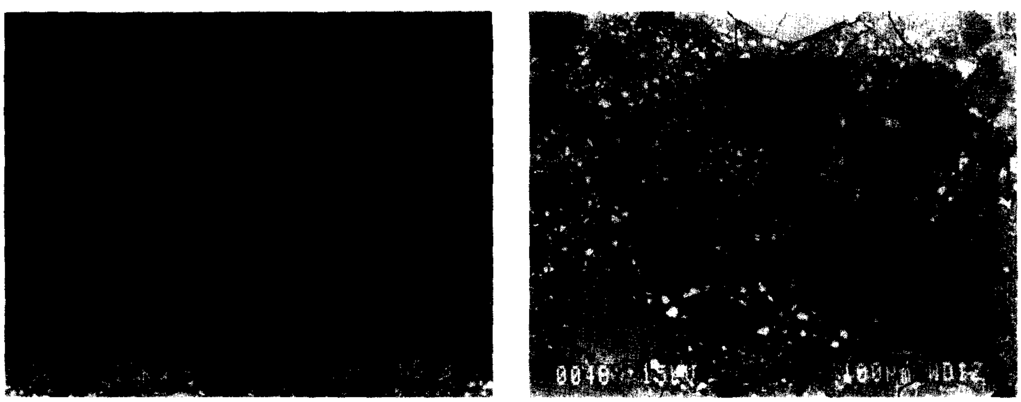

FIG.4 (a) and (b)
BSEI (50 X) 040-05 before and after freeze/thaw deterioration, cracks follow aggregate

"shadow effect" could also be seen when switching between SEI and BSEI modes on higher magnifications. The number of angular shaped defects was higher than in the sound concrete. The defects were mostly seen in connection with aggregate particles and cracks. It seemed as if parts of paste and aggregate particles had been ripped away next to cracks around aggregate particles, or in the paste where one crack divided into two forming a "Y". Figure 4 (b) shows a BSEI from 040-05 after frost deterioration (50 X).

<u>BSEI on self-healed concretes:</u>
At first sight, the healed specimens observed at 50, 300 and 1000 X resembled the ones taken directly after deterioration. The large cracks followed the same pattern and were, in general, of the same size. The number of voids and defects also, did not differ markedly from the specimens taken right after deterioration. The patterns of cracks of about 0.5 μm width seen at 300 and 1000 X did not seem to differ much from that observed in the other specimens neither. However, by following cracks at 300 and 1000 X, more unclear crack openings and deposits could be seen

at several locations. Most of the cracks still appeared open and empty, but at several points the crack openings and the edges of the cracks appeared more indistinct in accordance with the SEI observations on fracture surfaces. Figure 5 (a) and (b) show a detail of a partly self-healed crack on a polished section. Solids are seen in the crack on SEI, but on BSEI the crack appears almost empty, indicating that self-healing products are less dense than bulk paste. Also unreacted cement and the smallest type of cracks can be seen. The occurrence of these zones was rather randomly spread in the cracks, though most frequently in narrower cracks less than about 5 μm wide. The portion of healed cracks appeared rather small compared to the total crack volume. In non-resin filled cracks of about 0.5 μm, no such observations were made. From the inspections no clear difference in amount of re-hydration products between the two concretes could be seen.

EDXA spectra taken in re-hydration products revealed a similar type of composition as in bulk paste, with the 3 dominating peaks oxygen, silicium and calcium. In addition, EDX analysis performed in the cracks in the polished sections often showed relatively strong carbon peaks due to the resin. In a non-resin filled part of a crack of about 3 μm width in 040-05, a look into the depth of the crack (4000 X) revealed layered hydration products, as can be seen in figure 6. An EDXA spectrum revealed a very strong calcium-peak and no silicon, indicating that they consisted of calcium hydroxide.

Discussion

The present observations are in good agreement with the conclusions of previous studies (3, 12). Both investigations had indicated that the formation of rehydration products in cracks is possible. The present SEM-observations and EDX-analyses have shown that most of the rehydration products seen in the cracks were newly formed C-S-H. Ettringite and $Ca(OH)_2$ were also observed locally. The observations are also in agreement with the observed recovery of resonance frequency and compressive strength. The fact that cracks were only partly filled explain why the compressive strength recovery was so low. The large recovery in the non-destructive resonance frequency in spite of the low compressive strength recovery warrants further investigations. Since crack bridging by rehydration products was less evident in the widest cracks seen (approximately 10 μm), there might be a critical crack width beyond which self healing products are not able to

FIG.5 (a) and (b)

BSEI and SEI (1500 X) 040-00, rehydration products appear less dense in BSEI than in SEI

FIG.6
SEI (4000 X) 040-05, rehydration in part of crack (non-resin filled) in polished section

bridge cracks. The reason for the smaller self-healing in the silica fume concrete cannot be determined from these experiments. It is tempting to say that silica fume consumes more of the $Ca(OH)_2$ and therefore reduces the "self-healing potential" of the concrete compared to the OPC concrete. However, this investigation cannot support such a statement due to the differences in deterioration between the two concretes making direct comparison inappropriate, and the fact that self-healing and even $Ca(OH)_2$ was observed in self healed cracks also of the 040-05 concrete.

There are several of these observations that are not readily explainable. The shadow effect that appeared on crack edges when switching between BSEI and SEI on larger magnifications of the polished sections may indicate that crack edges were charged more by the electron beam than the adjacent paste. This might have affected the density of the back scattered electrons. Other possible explanations could be that the cement paste close to a crack is weakened due to large deformations at the rupture/separation of the crack. The shadow effect might, in that case, reflect a local reduction of the paste density. It is also possible that the paste along the cracks slanted up- or downwards. Such local changes of angle in the polished surface would reduce the density of the back scattered electrons detected.

Since the self healing gives a much smaller recovery of compressive strength than of the non-destructive resonance frequency, it is important to study the practical consequences of rehydration in frost induced microcracks. Some durability aspects and mass transfer processes are currently being investigated further by the authors on this question.

Conclusion

The microcracking of concrete due to freeze/thaw in water, and re-hydration ("self-healing") of cracks after subsequent storage of deteriorated specimens in water for three months have been studied by Scanning Electron Microscope (SEM). Two concretes of W/B = 0.40 and SF/B = 0 and 0.05 were investigated. SEM-investigations were performed on fractured surfaces and polished sections. Deterioration/healing (internal cracking) was measured by resonance frequency/dynamic modulus of elasticity and compressive strength. Freeze/thaw led to substantial loss in both resonance frequency and compressive strength. Subsequent self healing gave a substantial recovery of the frequency, but only a small recovery in compressive strength. After freeze/thaw deterioration the amount of cracks in the concrete was clearly increased. After self healing solid hydration products were seen traversing several cracks. At some points the re-hydration products bridging the cracks appeared rather dense judged by Secondary Electron Images (SEI). The occurrence of these healing products was less apparent in the concrete with SF than in the OPC concrete. Inspections by Back Scattered Electron Images (BSEI) on polished sections showed that the cracks formed on frost deterioration had widths of 1 - 10 μm. On the polished sections taken from the self healed specimens some cracks smaller than 5 μm were seen to narrow at several locations, and their appearance were less distinct due to solid products partly filling the cracks. On switching between SEI- and BSEI-modes, the solid products appeared less dense than the bulk cement paste. Energy Dispersive X-ray Analysis revealed that the composition was of C-S-H type, but also calcium hydroxide plate crystals and ettringite were observed.

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References

(1) Powers, T.C.: Proc. of the Highway Res. Board, V.29, pp.184-211 (1949)
(2) Powers, T.C. and Helmuth, R.A.: Proc. of the Highway Res. Board, V.32, pp.285-297 (1953)
(3) Vernet, C.: 8th. Int.Congr. on the Chemistry of Cement, Theme 4 Vol. V, pp.121-128 (1986)
(4) Pigeon, M. and Regourd, M.: Durability of Building Materials V.4, No.1, pp. 1- 19 (1986)
(5) Kukko, K.: VTT publications 126, Finland (1992)
(6) Fujii, T. and Fujita, Y.: CAJ Review, pp. 94-97 (1986)
(7) Stark, J., Ludwig, H-M.: RILEM TC 117 FDC, Res. seminar, Lund Inst. of Tech. Rep. TVBM-3048, pp.137-151, Sweden (1992)
(8) Abrams, A.: Concrete V.10, p.50, August (1925)
(9) Øfjord, A.: Betongen i dag V.19, No.3, p.57, Norway (1954)
(10) Munday J.G.L., Sangha C.M., Dhir R.K.: Proc. First Australian conf. on engineering materials, University of NSW (1974)
(11) Abdel Jawad, Y., Haddad, R.: Cem. Conc. Res. Vol.22, pp.927-936 (1992)
(12) Mor, A., Monteiro, P.J.M., Hester, W.T.: Cem. Conc. Agg., V.11, No.2, pp.121-125 (1989)
(13) Sellevold, E.J., Jacobsen, S., Bakke, J.A.: The International Workshop on Freeze-Thaw and Deicing Salt Scaling Resistance of Concrete, Laval University, pp.155 - 165, Canada (1993)
(14) McHenry D. and Brewer H.W.: PCA-bulletin 5A, pp.272-9-272-12 (1946)
(15) Jacobsen, S.: PhD-thesis in prep., Norwegian Institute of Technology (1995)
(16) Jacobsen S. and Sellevold E.J.: Consec'95 - Int. Conf. on conc. under severe conditions, Sapporo, Japan, Ch. and Hall (1995) (to be published)
(17) Diamond, S.: Conference in Tribute to M. Regourd, Sherbrooke, Canada, 19 p. (1994)
(18) Hornain, H.: Conference in Tribute to M.Regourd, Sherbrooke, Canada, 31 p. (1994)
(19) Ollivier, J.P.: Cem. Conc. Res. V.15 No.6, pp.1055-1060 (1985)
(20) Scrivener, K.L. and Pratt, P.L.:Proc.1st Int. Rilem Cong., V.1 pp.61-68, Ch.and Hall (1987)
(21) Kjellsen, K., Detwiler, R. and Gjørv, O.E.: Cem. Conc. Res. V.20, No.6, pp.927-933 (1990)
(22) Kjellsen, K., Detwiler, R. and Gjørv, O.E.: Cem. Conc. Res. V.21, No.1, pp.179-189 (1991)
(23) Holen, R.: SEM, report 5.11 High strength concrete Materials development, STF70 A92056, 69 p. 1992 (In Norwegian with English summary)
(24) Jacobsen, S., Gran, H.C., Sellevold, E.J., Bakke J.A.: High Strength Concrete - freeze/thaw testing and cracking, paper submitted for publ. in Cem. Conc. Res.