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Experimental identification of ice formation in small concrete pores

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Abstract

Freezing of water or salt solution in the concrete pores may be the cause for severe damage and significant reduction of service life. Although being one of the main research subjects during the past decades, a complete understanding of the deterioration mechanisms is still missing. This is probably because of a lack of understanding in the freezing of a liquid solution in the very small (some 10 nm) pores. In a series of experiments, the freezing process, its initiation, continuation and the resulting damage, was studied. Calorimetric, expansion and acoustic (ultrasonic pulse transit time, acoustic emission) methods were applied to monitor heat release, mechanical deformation and damage during a series of frost cycles. The results give an insight into supercooling, salt segregation, ice front penetration and thawing characteristics. Based on these data, a qualitative sequential damage model is proposed.

Keywords: Freezing and thawing; Calorimetry; Acoustic emission; Expansion; Durability

1. Introduction

The frost and frost deicing salt resistance of concrete and its testing belong to the most studied research topics worldwide. Nevertheless, many essential questions have not been answered so far. For instance, no sufficient explanation has been given why scaling and internal damage of concrete is much more severe when applying a liquid layer on the concrete surface and why damage increases at least one order of magnitude reaching a maximum at medium concentrations (3% for sodium chloride) when a salt solution is applied instead of pure water. Another important point that lacks explanation is the relationship between laboratory testing and on-site behavior of concrete. The application of new concrete mix designs on the basis of new additives and admixtures and the ongoing standardization of test procedures give this interesting topic an additional importance. To identify the damage mechanisms on site as well as in laboratory tests, a series of analytical experiments was carried out. The ice formation and the resulting damage formation were studied.

2. Experimental studies

The freezing and melting point of a pore solution is depressed through the dissolved ions, and because the liquid in smaller pores is due to surface interactions at a lower energy level than bulk water. Relations between pore diameter and freezing/melting point can be derived from thermodynamic models [1,2]. Furthermore, the pore shape influences the curvature of the liquid–ice interface and hence, the phase transition.

Ice formation can be observed directly through the induced changes in physical properties of the colloidal system or the heat release (enthalpy of fusion). The 9% volume increase upon phase transition and the induced damage are also detectable. In the presented study, ordinary Portland cement concretes with w/c ratios 0.45, 0.5 and 0.63, with and without air entrainment, were studied at an age of 1–2 years [3].

2.1. Calorimetry

The heat flow induced by the phase transition was measured by calorimetric methods. The calorimetric result of specimens at different degrees of saturation (20 °C) is plotted in Figs. 1 and 2. In saturated conditions, ice formation is observed just below 0 °C (saturated with water, external application of nucleating germs, specimen

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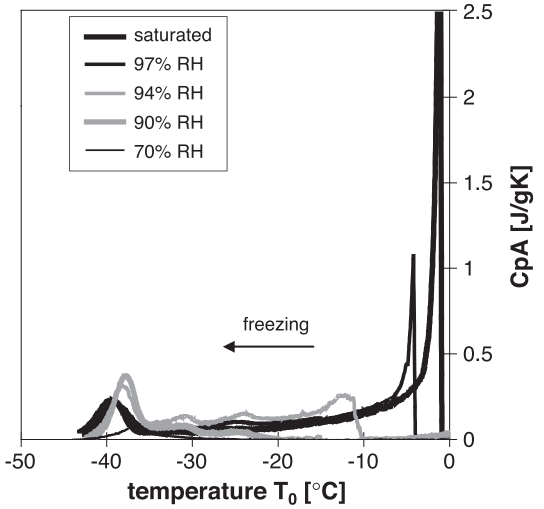

Fig. 1. Apparent heat capacity of concrete (w/c = 0.63) in function of saturation degree and specimen temperature (freezing).

dimension: 3 cm3). The lower the degree of saturation, so that according to Kelvin equation, just smaller pores remain saturated, the lower is the observed initial freezing point. For specimens saturated at 94% or 70% RH, the apparent heat capacity is increased in comparison to specimens at higher saturation degrees. This might be an indication for internal supercooling.

A well-marked freezing peak is observed near the homogenous nucleation temperature (− 40 °C), perhaps originating from strong supercooling in isolated pores. Upon thawing (Fig. 2), this peak is not found, and the released heat increases well in accordance with the saturation condition.

The hysteresis between freezing and thawing is much smaller than reported in literature [4,5]. This might be due to the use of relatively large concrete samples (instead of hardened cement paste) and externally applied ice nucleating germs [6] to avoid external supercooling. At least a part of the supercooling can be prevented by the external application of ice nucleating germs and the shape of the freezing curves differs significantly from the shape of the thawing curves. This supports the local supercooling theory [7]. A difference between freezing and melting point caused by the shape of the pores [8] seems to be of minor importance. Freezing nucleation seems to occur from a penetrating ice front rather than from spontaneous nucleation in the inner pore space.

When dry specimens are resaturated in a sodium chloride solution, the freezing/melting point is more and more depressed with increasing salt content (Fig. 3). For very high salt content, an additional peak at about − 20 °C, not far from the eutectic temperature, is observed. This peak, found for both freezing and thawing, might be the result of salt segregation. When an aqueous solution freezes, the ice crystals which are formed consist of almost pure water: the ions of the dissolved salt hardly are incorporated into the condensed phase. The concentration of the salt within the ice depends on the growth rate and the temperature of the ice surface. By the displacement of the salt through the advancing ice, a layer of increased salt concentration at the interface of the phases results [9].

2.2. Ultrasound pulse transit time

The pulse velocity in a porous specimen is significantly increased when its pore water freezes. This is due to the very different longitudinal wave velocities of 1485 m/s in water (20 °C/1 atm) and of 3828 m/s in ice Ih (0 °C/1 atm). This effect is used to monitor the beginning of ice formation in concrete blocks. A test arrangement with a liquid layer on top of the surface was chosen (Fig. 4) [10].

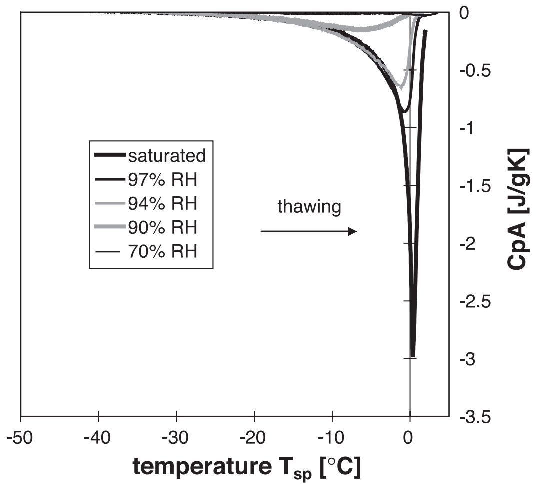

Fig. 2. Apparent heat capacity of concrete (w/c = 0.63) in function of saturation degree and specimen temperature (thawing).

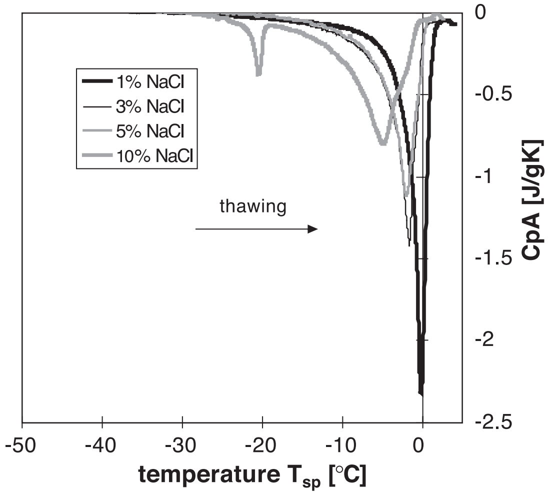

Fig. 3. Apparent heat capacity of resaturated (from 70% RH) concrete (w/c = 0.63) in function of salt content (mass %) of resaturation liquid and specimen temperature (thawing).

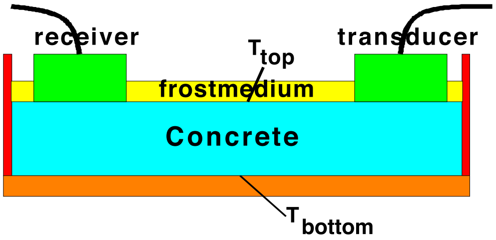

Fig. 4. Test arrangement.

The transit time between a transducer and a receiver is measured and can be roughly allocated to the amount of frozen water.

$$t_u - t_f = V_i\left(\frac{1}{c_w} - \frac{1}{c_i}\right)$$

where $t_{u/f}$, unfrozen/frozen transit time; $c_{w/i}$, sound velocity in water/ice and V_i, amount of frozen pore water.

As the pulse velocity within the concrete is much higher than the one of ice, the superficial frost medium (water, salt solution) is not influencing the result. Test results of an air-entrained frost resistant concrete (w/c = 0.45, AP 2 vol.%) are shown in Figs. 5–7. The plates (25 × 25 × 5 cm) were water-saturated prior to test.

When water is applied as frost medium (Fig. 5) and without supercooling of the liquid layer on top of the specimen, a significant increase in pulse velocity is detected not before all frost medium is frozen (end of freezing plateau, time 3.2 h).

The situation is different if some supercooling of frost medium occurs (Fig. 6). In this case, the pulse velocity suddenly increases on nucleation of the liquid layer. The ice front seems to quickly penetrate the specimen at least to a certain extent. When macroscopic water is frozen, the velocity of crystallization is controlled by the rate at which the water molecules are built into the ice crystal lattice. Because of the liberation of the latent heat of crystallization, it also depends on the diffusion of heat in the vicinity of the growing interface. The velocity increases with about the square of the degree of supercooling [11], which explains the sharp pulse velocity rise. When all frost medium is frozen, a further increase of pulse velocity is observed. The ice front penetration seems to continue.

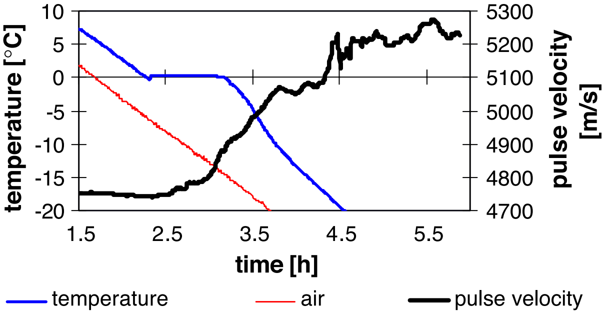

Fig. 5. Pulse velocity frost medium water without supercooling.

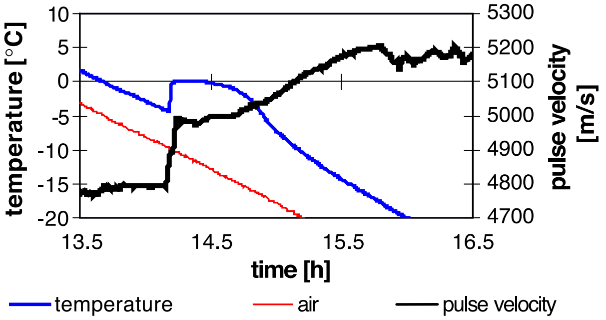

Fig. 6. Pulse velocity frost medium water with supercooling.

Applying a 3 mass % sodium chloride solution on the top surface gives a similar result as in the supercooled condition (Fig. 7). This supports local supercooling theory and external nucleation.

2.3. Expansion measurement

The ice formation and the damage evolution were studied by expansion experiments. To include liquid transport, a test arrangement with a liquid layer onto the specimen surface was chosen. Assuming that the solicitation near the surface is greatest, thin plates with 10-mm thickness were used. An increasing peak with increasing number of frost cycles (Fig. 8) was detected. This is probably due to an increasing saturation and progressive damage at each additional frost cycle. A similar behavior was also found in a special test arrangement, where the expansion perpendicular to the frost medium interface was measured [12]. A detail of the measured length change during one frost cycle with frost medium water and with frost medium 3% NaCl solution near the freezing point is plotted in Fig. 9.

When water is applied as frost medium and if some supercooling occurs, two different freezing peaks are observed: An instantaneous freezing peak at the moment when freezing is initiated (after a supercooling to about − 3 °C), which is followed by a progressive, slow expansion. The two peaks are separated by a temperature plateau, resulting from the exothermal phase transition of the superficial frost medium layer. Without a frost medium layer, both effects are superposed and cannot be distinguished experimentally.

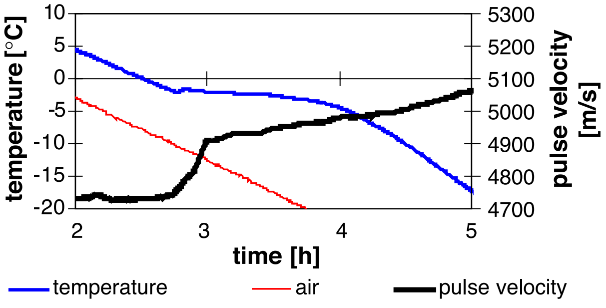

Fig. 7. Pulse velocity frost medium 3% sodium chloride solution.

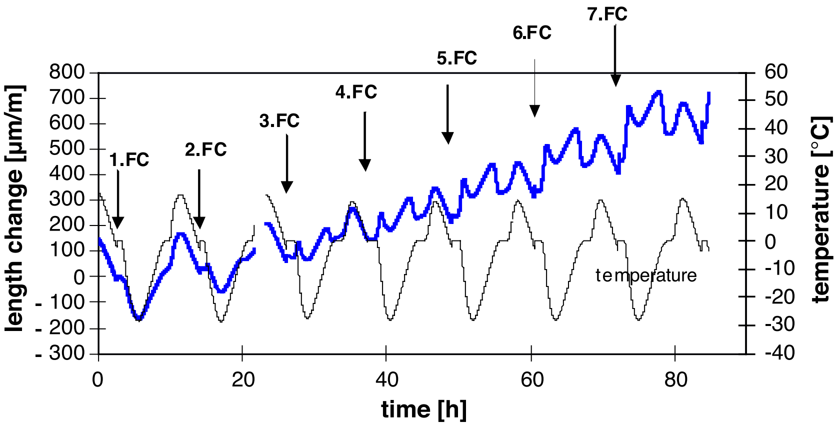

Fig. 8. Length change parallel to frost medium (3% sodium chloride) interface (w/c = 0.63).

A similar behavior is found when a salt solution as frost medium is applied. Supercooling is much reduced but nevertheless, the initial peak at the beginning of phase transition is dominant. The following progressive expansion is less pronounced. This indicates that with salts, a big part of the inner pore solution freezes very quickly when the ice formation is initiated at the outside.

2.4. Acoustic emission

To demonstrate that the observed length changes coincident with deterioration, the acoustic emissions of concrete plates with a frost medium layer (water, salt solution) on their surface were continuously monitored during the frost cycles. Acoustic emission intensity increased analogue to the observed expansion peaks. In particular, strong emission is observed when the frost medium layer supercools to some degrees (Fig. 10). If no supercooling occurs, emission is observed just beyond the freezing plateau when all frost medium already became ice. This demonstrates that the measured expansion causes damage. Strong and frequent emission was found near the freezing point of the applied frost medium but not at much lower temperatures. Unfortunately, it was not possible, even when applying source localization methods, to use this technique upon thawing, because of strong signal resulting from the cracking of the superficial ice layer (originating from the big expansion coefficient of ice).

3. Qualitative sequential damage model

From these experimental findings [3], one can conclude that freezing and thawing of a liquid in a pore system can be separated into five phases. Each phase is characterized by a specific temperature range and dominated by a different main damage mechanism (Fig. 11).

3.1. Phase 1: Freezing initiation, temperature range, 0 to −5 °C

The ice formation is initiated at the surface through ice nucleating germs, such as ice crystals, snow flakes, white frost, dust or aerosol particles or parts of a surface.

Most important at this stage is the ice formation rate. The faster the ice is growing, the bigger is the induced hydraulic pressure [13]. Critical values are just probable if supercooling (local or external) occurs. The presence of salt ions

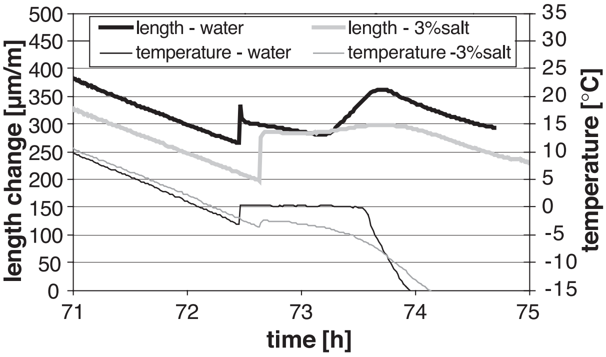

Fig. 9. Detail of length change near freezing point. (A) test with water, (B) test with 3% sodium chloride solution as frost medium (seventh frost cycle, w/c = 0.5).

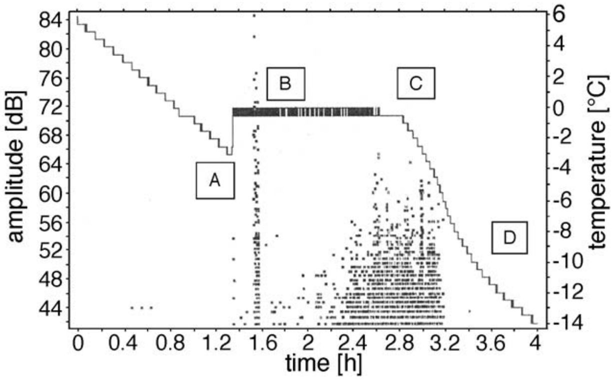

Fig. 10. Acoustic emission of concrete plate (w/c = 0.63) with frost medium water with external supercooling.

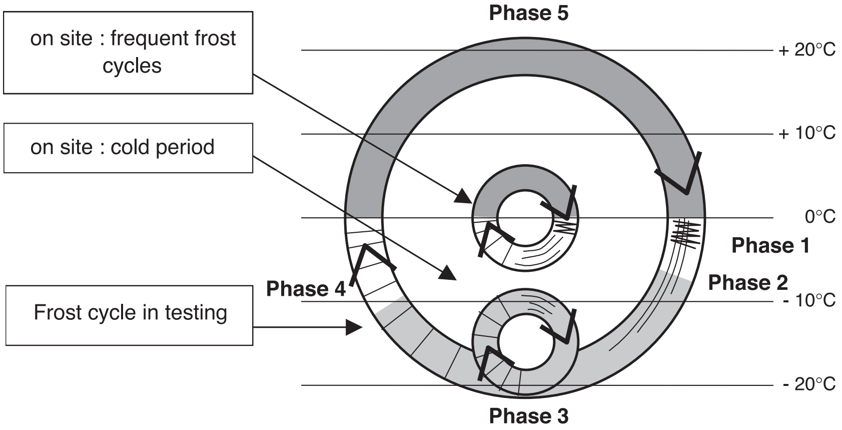

Fig. 11. Comparison of solicitation between on-site and laboratory test [17].

also causes rapid freezing probably owing to differences in freezing point between layers or salt segregation effects.

3.2. Phase 2: Penetration of the ice front, temperature range, 0 to −10 °C

Once the ice formation is initiated, the pore solution will freeze according to the freezing point which is related to the pore size and ion concentration. As freezing mostly is initiated from the preexisting ice (see Phase 1), an ice front penetrates the pore system. The pore water only freezes when the pore is connected to the surface through pores in which the pore solution freezes at a higher temperature than the actual one. The salt concentration may be increased locally owing to segregation of salt ions.

Local supercooling occurs if large pores or whole pore regions are connected to the ice front through smaller “neck” pores only. Especially highly porous border zones around aggregates and porous nonfrost resistant aggregates might be separated from the ice front through smaller cement matrix pores leading to high hydrostatic pressure [14] when reached by the ice front.

3.3. Phase 3: Redistribution of pore solution, temperature range, between −5 °C and minimum temperature of the frost cycle

The thermodynamic equilibrium in the pore solution is disturbed by the ice formation [15]. Due to the lower chemical potential, unfrozen pore solution, mostly in smaller pores or locally supercooled pore regions, flows towards the existing ice in the larger pores and freezes there. Liquid transport is also induced by a higher salt concentration ahead of the ice front (osmosis). This redistribution may induce internal shrinkage and additional hydrostatic pressures. In special experiments [3], however, no indications for damage of concrete at this phase were found. Redistribution of pore water may just be the prerequisite for the damage formation during the ongoing and the next frost cycle.

3.4. Phase 4: Thawing, temperature range, minimum temperature to 0 °C

Empty pore space, resulting from the bigger thermal contraction of ice than of the matrix, is refilled. At heating, the ice will expand more than the surrounding matrix, which induces additional tension. The tension is stronger, the lower the minimal temperature of the frost cycle is. It also depends on the efficiency of the redistribution of the liquid during the third phase [16] (Fig. 12).

3.5. Phase 5: Resaturation, temperature >0 °C

During the thawing phase above 0 °C, the additional pore space due to deterioration (cracks, etc.) is refilled from the outside with liquid. The degree of saturation, hence, is increased, especially at the predeteriorated critical spots.

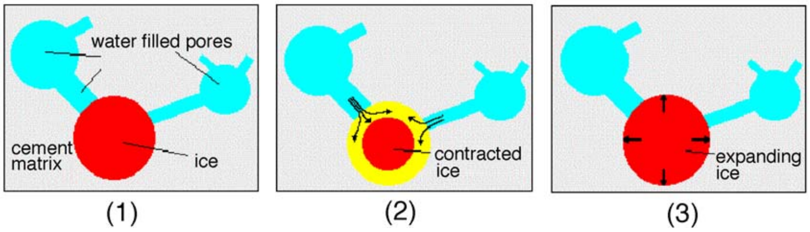

Fig. 12. Thermal contraction of ice when temperature lowers (1) and resaturation with pore solution which then freezes (2). This induces tension in the cement matrix when temperature rises again and the ice expands (3).

This is the prerequisite that the effect of a further frost cycle is intensified. In this phase, no damage is induced, but the resaturation is of big importance for the further behavior of the material. Experiments and on-site experience demonstrate that no further damage occurs if there is not enough liquid for a complete resaturation available.

All five phases contribute to the frost deicing salt deterioration. During a complete frost cycle (with thawing phase) and sufficiently low minimal temperature, all phases are active. The importance of each phase, however, depends on the pore size distribution and the climatic conditions.

Deicing salt has damage-increasing as well as damage-preventing components [3], depending on the salt concentration and the active phase. The sum of all these different effects probably makes the frost deterioration worse at a medium salt concentration.

At a real building, the most frequent frost cycles (50–70 per year) are induced by the night/day change. When the day maximum is above 0 °C, the minimal temperature at the surface of a huge building is hardly dropping below -5 °C. External supercooling is very unlikely because of the various sources for ice nucleating germs and the large surface. Therefore, only Phases 2 and 5 participate in the deterioration process [17]. A second typical case on site is the case of a cold period. The day/night temperatures at the building surface temperature cycle below 0 °C during many days. In this case, and also when no external water is available, Phase 5 is not active and the deterioration process will not be very effective. The full cycle (maximum >0 °C, minimum < -10 °C) is seldom and low temperatures on a building surface are just reached during a cold period.

In the laboratory frost resistance tests, the temperature cycle is complete, the minimum temperature is low enough and water is available. A fast test result is desired and hence, a strong solicitation is favored. However, the test methods may put different weights on the different phases. Fast or even shock freezing, for instance, attach too much significance to Phases 1 and 2. Hence, a big discrepancy between laboratory testing and on-site behavior exists, often described for concretes containing fly ash, for example. The damage mechanisms do not correspond exactly, and the frost resistance in laboratory tests is evaluated just approximately. However, a microstructure with a good behavior in the laboratory test will also show a good behavior on site, but not necessarily vice versa.

4. Conclusions

The phase transition of pore solution of cementitious materials in an open system, where the surface is exposed to water or a sodium chloride solution, has been studied, applying specially designed experimental methods. Many of these methods and test arrangements are used for the first time to the problem of frost damage and allow to study ice formation including supercooling effects and, to a certain extent, other effects like salt ion segregation. Ice formation in the studied system can be separated into two main phases: an instantaneous nucleation part and a progressive ice penetration (percolation) part.

Furthermore, it is demonstrated that big hysteresis effects between freezing and thawing can be partly avoided when ice nucleation is initiated through special ice formation germs (ice nuclei) or in a macroscopic liquid layer. This result obtained in calorimetric tests is also confirmed by ultrasonic pulse transit time experiments and supports a local supercooling theory. Comparing acoustic emission with expansion results closes the link between ice formation and nonthermal expansion on the one hand and resulting crack formation on the other.

A qualitative sequential model is proposed to explain the main experimental findings. The model distinguishes between five different phases, all related to a specific temperature range and a dominant damage mechanism. Each phase is important and contributes to the frost deicing salt deterioration. The different effects of the deicing salt are discussed.

The sequential model does not need to differentiate between on-site and laboratory damage mechanisms but predicts, based on the difference in solicitation, differences between laboratory and on-site behavior of cement-based building materials.

References

[1] M. Brun, A. Lallemand, J.-F. Quinson, Ch. Eyraud, A new method for the simultaneous determination of the size and the shape of the pores: the thermoporometry, Thermochim. Acta 21 (1977) 59–88.

[2] M. Setzer, Einfluss des Wassergehalts auf die Eigenschaften des erhärteten Betons, Deutscher Ausschuss für Stahlbeton, Heft 280 (1977) 1–96.

[3] J. Kaufmann, Experimental Identification of Damage Mechanisms in Cementitious Porous Materials on Phase Transition of Pore Solution under Frost Deicing Salt Attack, thesis EPF Lausanne No 2037 (1999).

[4] D. Bager, E. Sellevold, Ice formation in hardened cement paste: parts 1 + 2, Cem. Concr. Res. 16 (1986) 709–720, 835–844.

[5] R. Beddoe, M. Setzer, Änderung der Zementsteinstruktur durch Chlorideinwirkung, Forschungsberichte aus dem Bauwesen 48 (1990) 1–75 (Uni Essen).

[6] N. Fukuta, B. Mason, Epitaxial growth of ice on organic crystals, J. Phys. Chem. Solids 24 (1963) 715–718.

[7] G. Fagerlund, Non Freezable Water Contents of Porous Building Materials, Lund Institute of Technology, Sweden, 1974, Report 42.

[8] M. Setzer, Freeze thaw and deicing salt resistance combined with water and chloride uptake, in: K. Watanabe (Ed.), . BRI-Proc. Int Conf. on Mass-Energy Transfer and Deterioration, Paris, France, BRI Proceedings No. 2. (1995) 25–35.

[9] C. Tilby, H. Erdmann, D. Langbein, H. Behret, Transportvorgänge in der Grenzschicht bei Lösungskristallisation unter Mikrogravitation-Wachstum von Eis in wässrigen Lösungen, Forschungsbericht W-84-031 Luft und Raumfahrt, Batelle Inst. e.V. Frankfurt (1984).

[10] J. Kaufmann, Study of ice formation with ultrasonic pulse transit time measurement, in: J. Janssen, et al (Ed.), Proc. RILEM Workshop on Frost damage in Concrete Minneapolis, USA, RILEM Publications s.a.r.l., 2002, pp. 161–172.

[11] H. Pruppacher, On the growth of ice contained in capillaries, Z. Naturforsch. 22a (1967) 895–901.

[12] J. Kaufmann, W. Studer, Length changes of concrete specimen during frost deicing salt resistance test, in: M. Setzer, R. Auberg (Eds.), Proc. RILEM Workshop on Frost Resistance of Concrete, Essen, Germany, E&FN Spon, 1997, pp. 212–221.

[13] T.C. Powers, R.A. Helmuth, Theory of volume changes in hardened cement paste during freezing, Proc. Annu. Meet. - Highw. Res. Board 32 (1953) 285.

[14] G. Fagerlund, Internal frost attack—State of the art in frost resistance of concrete, in: M. Setzer, R. Auberg (Eds.), Proc. RILEM Workshop on Frost Resistance of Concrete, Essen, Germany, E&FN Spon, 1997, pp. 319–338.

[15] G. Scherer, Crystallisation in pores, Cem. Concr. Res. 29 (1999) 1347–1358.

[16] P. Grübl, Über die Rolle des Eises im Gefüge zementgebundener Baustoffe, Beton 31 (H. 2) (1981) 54–58.

[17] J. Kaufmann, W. Studer, Schadensmechanismen bei der Frost–Tausalzbean-spruchung von Beton, report 81/95 Nr. 548 Swiss federal road office (2000).