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Air void structure and frost resistance – a challenge to Powers' spacing factor

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Abstract This article compiles results from 4 independent laboratory studies. In each study, the same type of concrete is tested at least 10 times, the air void structure being the only variable. For each concrete mix both air void analysis of the hardened concrete and a salt frost scaling test are conducted. Results were not originally presented in a way, which made comparison possible. Here the amount of scaled material is depicted as function of air voids parameters: total air content, specific surface, spacing factor, and total surface area of air voids. The total surface area of air voids is proportional to the product of total air content and specific surface.

In all 4 cases, the conclusion is concurrent that the parameter of total surface area of air voids performs equally well or better than the spacing factor when linking air void characteristics to frost resistance (salt frost scaling). This observation is interesting as the parameter of total surface area of air voids normally is not included in air void analysis.

The following reason for the finding is suggested: In the air voids conditions are favourable for ice nucleation. When a capillary pore is connected to an air void, ice formation will take place in the air void, being feed from the capillary, but without pressure build-up in the capillary. If the capillary is not connected to an air void, ice formation will take place in the capillary pore, where it can generate substantial pressure. Like this, frost resistance depends on that capillary pores are connected to air voids. The chance that a capillary pore is connected to an air void depends on the total surface area of air voids in the system, not the spacing factor.

Keywords: *Air void structure – spacing factor – salt frost scaling – frost resistance*

1. Introduction

In 1975, Powers (1975) summarized 40 years of research related to concrete frost resistance. He emphasised the importance of entrained air; concrete needs a “sufficient concentration of air bubbles” to be immune to frost damage. Today, this statement is generally accepted and it is very well documented, see for example the reference list in the book “Durability of concrete in cold climates” by Pigeon and Pleau (1995). However, it is still a challenge to translate “sufficient concentration of air bubbles” into a quantitative requirement in a concrete specification. The problem is to identify a measurable air void parameter, which has a definite relation to degree of damage during freeze/thaw action, and where a limit value can be identified.

When an engineer encounters a problem, no matter the field of engineering, the first choice of method to solve it is normally a deductive method: The engineer goes through a series of forward-looking actions to recognise the problem, identify basic variables, and develop ways to perform measurements. Finally, after planning and carrying out measurements, it is possible to evaluate the results (Vincenti, 1990). Hopefully the investigation has lead to new insight, based on which it is possible to solve the problem. A historian would do just the opposite. He or she looks backward in time and gain new insight by identifying general trends in isolated incidents in the past. Like this, the work method of a historian is inductive.

The scope of the present work is to approach the difficulty in relating frost resistance to characteristics of the air void structure with an inductive method. No new experiments are designed and executed in this work. Instead, already existing data from the literature on salt frost scaling and air void structure is reviewed to identify trends with general validity.

2 Theory

Traditionally, it is assumed that the spacing factor proposed by T.C. Powers (1949) is an appropriate way to describe the air void structure, so demands are formulated as limits for the maximum spacing factor, possibly in combination with limits for minimum total air content.

Powers spacing factor was put forth as a logical result of the hypothesis about hydraulic pressure as the cause of damage during frost action, which also has Powers as progenitor (Powers 1945): When liquid water transforms to ice, its volume increases, and therefore unfrozen water is expelled from the place of ice formation. This liquid flow generates hydraulic pressure in the pores, which can damage the concrete. The pressure build-up among other things depends on the flow length to a free surface. If all points in the cement paste are adequately close to a free air void surface, then damage cannot occur. Powers' spacing factor L is an estimate of the longest distance to an air void surface. It is calculated in the following way (Powers 1949):

$$L = \begin{cases} \frac{p}{A} \cdot \frac{1}{S} & \text{for } \frac{p}{A} < 4.342 \\ \frac{3}{S} \left(1.4 \left(\frac{p}{A} + 1 \right)^{1/3} - 1 \right) & \text{for } \frac{p}{A} \geq 4.342 \end{cases} \quad (1)$$

Where

- p is the paste content [% of concrete volume]
- A is the air content [% of concrete volume]
- S is the specific surface [mm^{-1}]

The hydraulic pressure hypothesis is only one among several theories on what happens during frost action, and several researchers have questioned its validity. Powers himself, several years after he put forth the hypothesis, ended up supporting another theory: the hypothesis about microscopic ice lens growth,

1 where unfrozen water moves to the freezing site instead of away from it (Powers
2 1975). Despite of this, the spacing factor is still a very popular evaluation
3 criterion. Though it may be without sound theoretical foundation, the spacing
4 factor is one of few attempts to quantify the air void structures ability to provide
5 protection against frost deterioration, and in many cases, it points in the right
6 direction. If for example trial casting reveals inadequate frost resistance, then frost
7 resistance can be improved by decreasing the spacing factor, typically by
8 increasing the dosage of air entraining agent. However, there may be better ways
9 to benchmark the air void structure, which are yet to be discovered. For example,
10 results published by Lindmark (2000; 2010) and Hasholt and Clemmensen (2010)
11 have independently of each other indicated that the amount of surface scaling in
12 an accelerated freeze/thaw test depends on the total surface area of air voids. The
13 total area of air voids [m^2/m^3 concrete] is proportional to the product $S \cdot A$, where S
14 is the specific surface and A is the total air content as explained in equation 1.
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28 **3. Experimental results from literature**

29 This paper presents 4 different experimental studies, which include air void
30 analysis on hardened concrete as well as freeze-thaw testing (salt frost scaling).
31 Originally, the studies had different objectives. Therefore they varied the air void
32 structure by other means than just changing the dosage of air entraining agent.
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- applying different procedures when vibrating the concrete (Backstrom et al. 1958b)
- using different commercial air entraining agents without or in combination with other chemical admixtures (Siebel 1989; Petersson 1989)
- applying pressure during hardening (Jensen 2005)

This article examines the relation between salt frost scaling resistance and the classical air void parameters: total air content A , specific surface S and spacing factor L . It also examines the relation between salt frost scaling resistance and total surface area of air voids. The later is also an air void parameter, but it is seldom registered. However, as mentioned in section 2, observations indicate that

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it may be relevant for the concrete frost resistance, and therefore this air void parameter is also examined.

3.1 Study 1: Effect of compaction (1958)

Background

In the 1950's, the use of air entraining admixtures was relatively new, and there were still many questions on how to obtain an adequate air void structure, which can ensure frost resistance. In 1958 Mielenz and colleagues published a series of 4 papers, dedicated to explaining how air entraining agents function. Part 1 focuses on how air voids are created during mixing, and how the air void structure can change in the fresh concrete up to the point of setting (Mielenz et al. 1958a). Part 2 demonstrates how different air entraining agents leads to air void systems with different characteristics such as total air content and different air void size distribution (Backstrom et al. 1958a). Part 3 illustrates how other factors can influence the resulting air void structure and frost resistance of air entrained concrete, e.g w/c, compaction, sand grading, and temperature (Backstrom et al. 1958b). In part 1-3, all concrete mixes are prepared in the laboratory. In part 4, the findings in the previous parts are confirmed for concrete in real structures (Mielenz et al. 1958b). This series of papers has become classical and newer literature often uses them as references, as this is a very thorough study.

Content of experimental work

In the study by Mielenz and colleagues, expansion test was the preferred method for freeze/thaw testing. For this purposes, specimens were cast with inserts for length change measurements. However, for a reason not mentioned, test specimens made with different compaction regimes were cut from cast cylinders, and they were therefore missing inserts. Instead, a kind of scaling test was performed, where specimens were exposed to cycles of freezing and thawing until they had lost 25% of their mass (Backstrom et al. 1958b).

Tests were carried out for 3 concrete mixes. The mixes were similar (same type of aggregates, same w/c = 0.50), but they had different dosages of air entraining agent, leading to different air contents in the fresh concrete (3.0%, 6.5%, and

1 8.8% measured with a pressure method). The fresh concrete was cast in cylinders,
2 2 cylinders for each of the following vibration times: 2, 6, 12, 20, 30, and 50
3 seconds. Like this, 18 different air void systems were tested.
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7 **Results**

8 The results are shown in Fig. 1:
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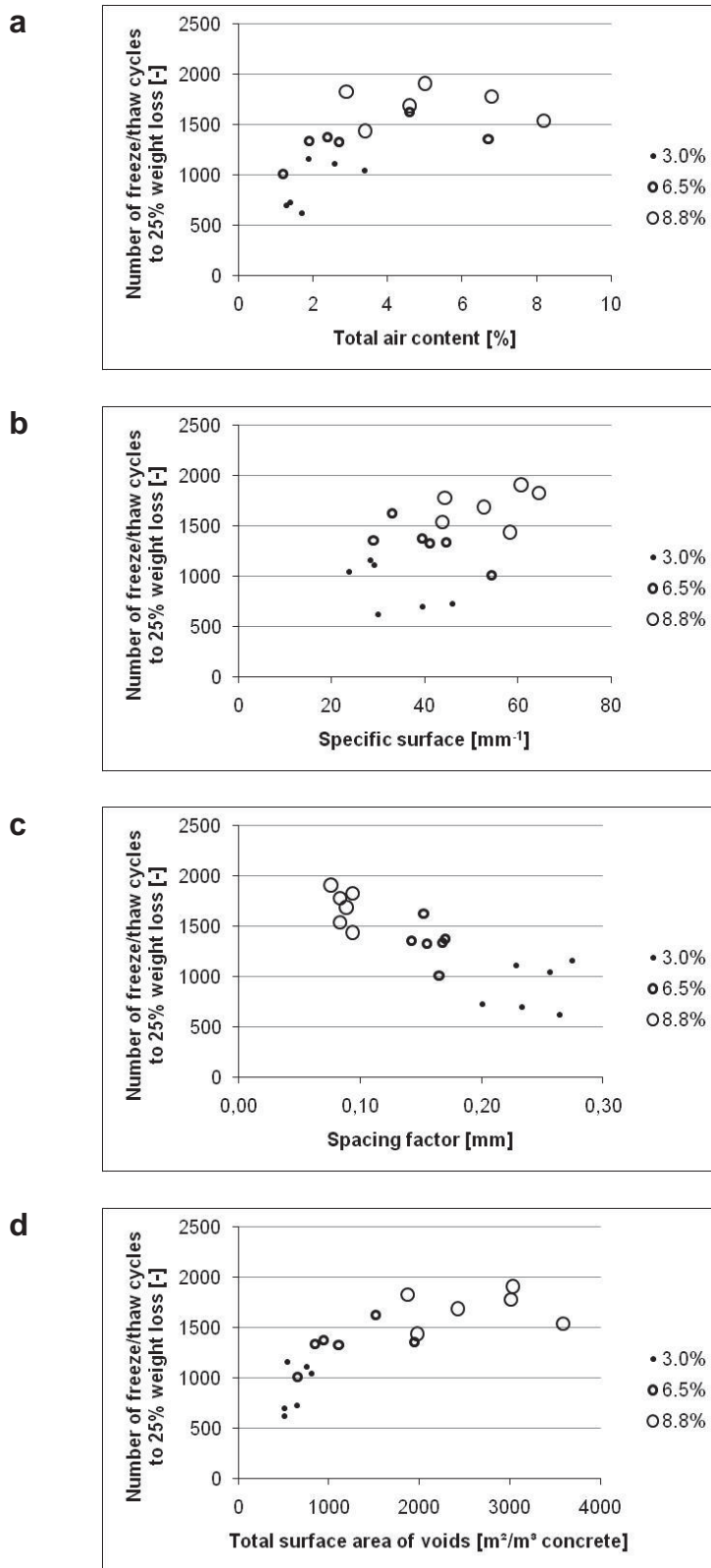


Fig. 1 Salt frost scaling resistance (number of freeze/thaw cycles to 25% weight loss) shown as function of (a) total air content, (b) specific surface, (c) spacing factor, and (d) total surface area of air voids. Data were originally published by Backstrom et al. (1958b). The study comprised 3 different concrete mixes with 3.0%, 6.5%, and 8.8% air in the fresh concrete, and for each mix 6 different compaction regimes were applied.

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When studying the relation between scaling and spacing factor in Fig. 1c, the data points related to the 3 basic mixes looks like 3 distinct populations. In the mixes with initial air contents of 6.5% and 8.8%, vibration does not change the spacing factor very much. For the 6.5% mix, the difference between maximum and minimum spacing factor is 0.03 mm, and for the 8.8% mix, the difference between maximum and minimum spacing factor is only 0.02 mm, which is comparable to the uncertainty of the test method. But despite the almost unchanged spacing factor, the rate of scaling is changed for different vibration regimes. For example for the 6.5% mix, the most freeze/thaw resistant specimens withstand 60% more freeze/thaw cycles before 25% mass loss is reached than the specimen with poorest freeze/thaw resistance. The specimens with poorest freeze/thaw resistance have been vibrated for the longest time, but they only have the third largest spacing factor in this group. It is also noted in the original paper that the relation between spacing factor and scaling is not consistent.

When studying the relation between scaling and total surface area of air voids in Fig. 1d, all 18 data points from the 3 basic mixes look like they belong to the same population. The specimens are prepared under laboratory conditions where mix proportions can be very well controlled, so it is unlikely that e.g. unintentional variations in w/c can cause differences between mixes. Presumably, the only difference between specimens is their air void structure. Therefore, when plotting a measure of freeze/thaw resistance against the decisive air void parameter, it is reasonable to expect a continuous curve. Therefore the results of Mielenz and colleagues indicate that total surface area of air voids is a better parameter to describe how well an air void system protects the concrete against freeze/thaw attack.

3.2 Study 2: Combination of different admixtures (1989)

Background

In the 1980's, superplasticizers for concrete were an emerging technology. In West Germany, concrete for freezing environments was approved from data on mix composition and air content measured in the fresh concrete. The air void structure in the hardened concrete only had to be examined in cases of doubt. The

1 early research on concrete with superplasticizing admixtures and frost resistance
2 was contradictory, but some of the reports indicated that superplasticized concrete
3 had coarser air void structure and therefore larger spacing factor than concrete
4 without superplasticizing admixtures with similar air content. This would imply a
5 risk that the limits for minimum air content in fresh concrete based on experience
6 with concrete without superplasticizing admixtures would be too low for concrete
7 containing superplasticizers. For this reason, the Research Centre of the German
8 Cement Industry (VDZ) commenced a research project on frost resistance of
9 superplasticized air-entrained concrete (Siebel 1989).
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18 **Contents of experimental work**

19 The work presented by Siebel (1989) comprised 4 different test series. Within
20 each series, cement type, cement content, w/c, and type of aggregates were
21 unchanged, but the mix was produced with varying dosages of air entraining agent
22 and with varying dosages of superplasticizing agents. In 2 of the test series (w/c =
23 0.45), both air content in fresh concrete, air void structure in hardened concrete
24 (according to ASTM C 457), and freeze-thaw resistance in a standardised test
25 were investigated. The freeze-thaw test was a method developed at the research
26 centre carrying out the investigation; 10 cm cubes were immersed in 3% NaCl,
27 where they were frozen to -15°C and thawed in repeated cycles, and after 100
28 cycles, the mass loss was registered (if the mass loss was less than 5%, the
29 concrete mix was considered frost resistant).
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43 **Results**

44 In the paper by Siebel (1989), results are only presented graphically. According to
45 personal communication with E. Siebel, retired head of Department for Material
46 Technology at VDZ, and Christoph Müller, present head of Concrete Technology
47 Department at VDZ, the original laboratory records unfortunately no longer exist.
48 Therefore, the results presented in Fig. 2 are based on manual readings from
49 graphs in Siebel's original paper, where individual data points are plotted for each
50 mix. The accuracies on readings are:
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- total air content A : $\pm 0.1\%$
- spacing factor L : ± 0.01 mm
- scaling (mass loss in %): $\pm 0.2\%$

The specific surface S is calculated by using the paste content (mix design stated in the original paper) together with the manual readings of total air content A and spacing factor L as input parameters.

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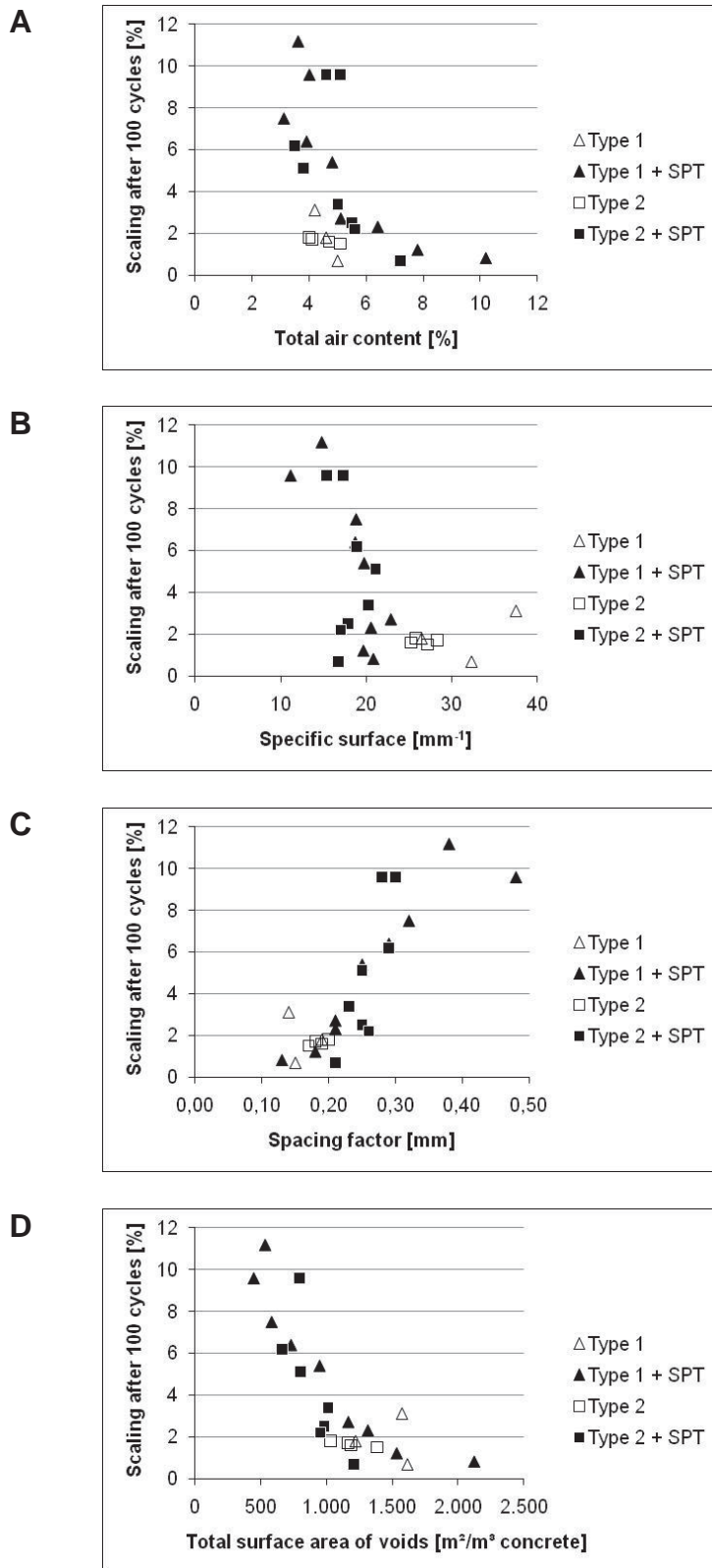


Fig. 2 Salt frost scaling as function of (a) total air content, (b) specific surface, (c) spacing factor, and (d) total surface area of air voids. Data were originally published by Siebel (1989). The 4 test series represent different combinations of admixtures (air entraining agent type 1 or type 2, with or without a superplasticizing agent). In each series, the dosage of air entraining agent is varied.

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It can be seen that for non-frost resistant concrete mixes, where mass loss after 100 freeze/thaw cycles exceeds 5%, there is a large scatter in Fig. 2c, where mass loss is plotted vs. spacing factor. The scatter is smaller in Fig. 2d, where mass loss is plotted vs. total surface area of voids. The same mass loss of approximately 10% is obtained for 3 mixes with spacing factors varying from 0.28 to 0.48 mm. Here the spacing factors indicate that there should be a difference in frost resistance, but this is not confirmed by the measurements of mass loss.

3.3 Study 3: Mix optimisation (1989)

Background

The study of Petersson (1989) was based on trial mixes aimed at finding a good mix design, which at the same time produced:

- concrete with high compressive strength (a minimum cube strength of 45 MPa)
- concrete with cement content not exceeding 400 kg/m³ concrete
- concrete with good salt-frost resistance
- concrete with good workability (slump 75-85 mm)

Like this, the starting point of the study of Petersson was a classical dilemma in concrete technology: High strength demands low w/c. If cement is the only powder, low w/c leads to high cement content or to poor workability, if the cement content is fixed at a certain, acceptable level. Introducing a superplasticizing admixture can be the answer on how to achieve high strength with minimum cement content. However, addition of a superplasticizer may have negative side effects: It may make air voids coarser, so the concrete becomes more prone to show salt frost scaling, and it may increase the total air content, so the strength is reduced.

The study by Petersson (1989) was performed, when superplasticizers were relatively new, and therefore documentation was needed on how these contradictory demands could be met. As the study also addressed the

1 compatibility between different concrete admixtures, the study of Petersson had
2 common features with the study by Siebel presented in the previous section.
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5 **Contents of experimental work**

6 The study comprised 3 test series:
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- 10 • *AEA1*: Air entraining agent 1 (mixture of neutralized vinsol resin and
11 synthetic tenside) used as only additive
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- 13 • *AEA2*: Air entraining agent 2 (neutralized vinsol resin) used as only
14 additive
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- 16 • *AEA1 + PL*: Air entraining agent 1 used in combination with a melamine
17 based plasticizing agent
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25 In each test series, w/c and slump was kept constant (0.45 and 75-85 mm,
26 respectively). Mixes were prepared with target air content in fresh concrete of 3,
27 4, 5 and 6 %. The air content was varied by varying the dosage of air entraining
28 agent. To keep the slump constant, the paste content was varied. When using a
29 plasticizing agent, the amount relative to cement mass was constant
30 (recommended dosage).
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38 The air void structure in the hardened concrete was studied using microscopic
39 analysis of thin sections. Freeze-thaw testing was carried out according to SS 13
40 72 44 (1988).
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45 **Results**

46 Results are shown in Fig. 3.
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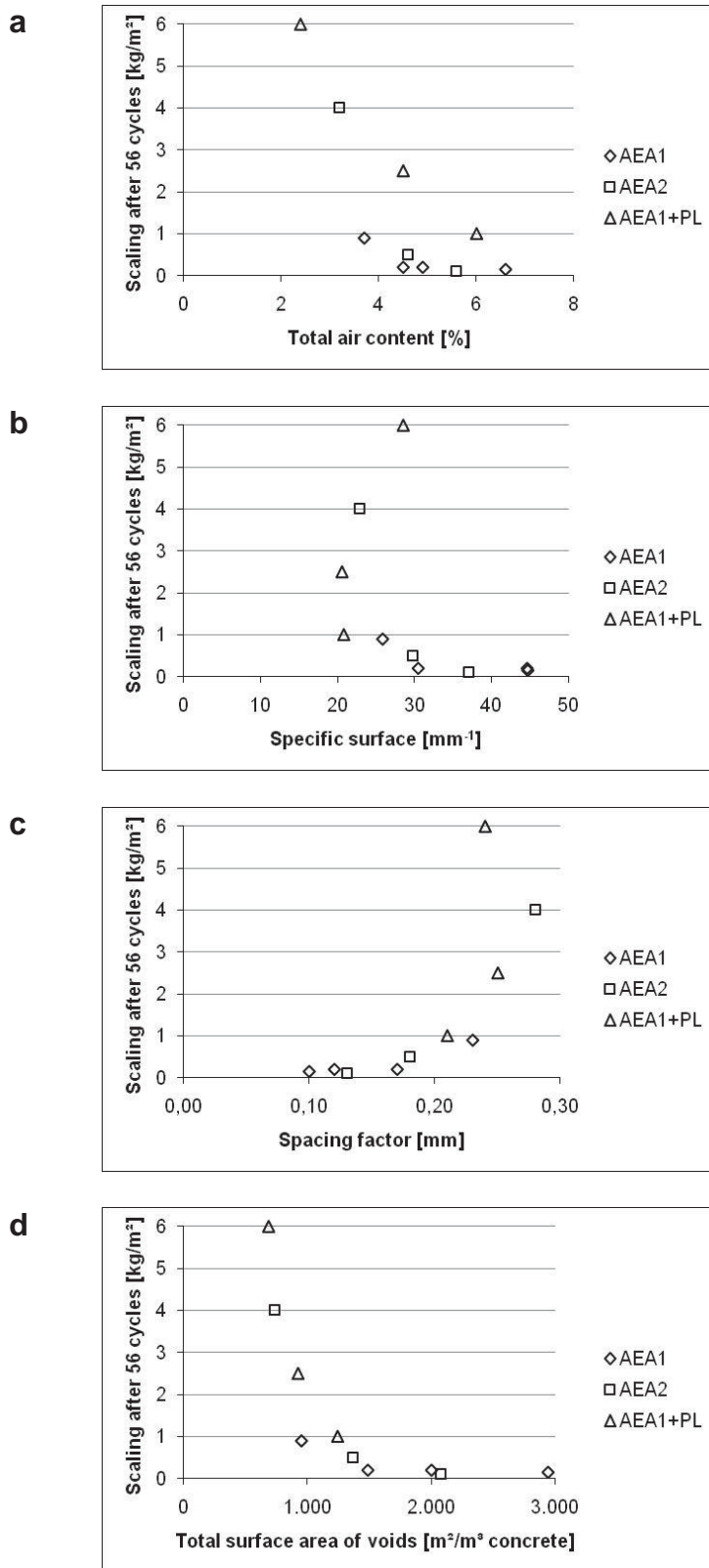


Fig. 3 Salt frost scaling as function of (a) total air content, (b) specific surface, (c) spacing factor, and (d) total surface area of air voids. Data were originally published by Petersson (1989). The test series represent different combinations of admixtures. Note: the specific surface is not stated in the original paper, so here it is calculated from the spacing factor.

1 According to the test method, the frost resistance is acceptable, if the amount of
2 scaling after 56 cycles does not exceed 1 kg/m². Only 3 of the tested mixes do no
3 exhibit acceptable scaling results.
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7 In Fig. 3a some dependence between total air content and scaling is observed, but
8 for the same air content, the scaling is significantly higher for the series with
9 superplasticizer, AEA1+SP, than for the other 2 series. In Fig. 3b there seems to
10 be no relation between scaling and specific surface.
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16 The correlation between on one hand scaling and spacing factor and on the other
17 hand scaling and total area of voids seems equally good (qualitative judgement).
18 However, the 3 points in the upper tail of the spacing factor curve in Fig. 3c are
19 not in a logical order. It is expected that the highest spacing factor induces the
20 highest amount of scaling, but this is not the case. In Fig. 3d, where scaling is
21 mapped as function of total area of voids, the same 3 points are placed in expected
22 order, where scaling decreases when the surface area of voids increases.
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32 **3.4 Study 4: Effect of pressure during hardening**

33 **Background**

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35 With the good workability of self-compacting concrete, castings can be performed
36 very fast. When casting for example tall walls, a high pressure will be generated at
37 the bottom of the wall resulting in compressed air voids. Therefore it can be
38 difficult to meet demands on e.g. a total air content of 5%, and changes of the air
39 void structure can be an unpleasant surprise if all pre-testing has been performed
40 on unloaded concrete such as cast cylinders.
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49 This was the starting point for a M.Sc. thesis work (Jensen 2005). The primary
50 objective of the project was to study the influence of increased hydrostatic
51 pressure during hardening on the air void structure. The experimental data were
52 used to test if it was possible to predict the air void size distribution in concrete
53 hardened under pressure, when using the air void size distribution in unloaded
54 concrete as input for calculations. Calculations were based on Boyle-Mariottes
55 law (saying that for an ideal gas at constant temperature the product of pressure
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1 and volume is constant). These results were published by Jensen et al. (2005). A
2 secondary objective of the project was to get an indication on how pressure
3 related changes of the air void structure would change the frost resistance. Results
4 related to the secondary objective are here published for the first time.
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9 **Contents of experimental work**

10 The concrete used for testing was a self-compacting concrete with $w/c = 0.35$
11 (CEM I cement and no additional powders).
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16 Fresh concrete was placed in plastic bags (because of the flow properties of the
17 concrete, placement was possible without vibration). Sealed plastic bags were
18 immediately placed in water in containers, where pressure then was applied for 24
19 hours.
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25 Concrete mixes were prepared with 2 different dosages of air entraining agent.
26 The low dosage equalled 0.10% and the high dosage equalled 0.25% of cement
27 mass. Each mix was placed in 4 different containers with pressures of 1, 1½, 2,
28 and 2½ bar. Castings with each dosage of air entraining agent were repeated 3
29 times (mix 1, mix 2 and mix 3), resulting in a total of 24 specimens with different
30 air void structures.
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38 Air void analysis was performed according to DS/EN 480-11 (1999) using an
39 automatic camera system. Freeze-thaw testing was performed according to the
40 reference method of prENV 12390-9 (2003). However, the size of each test
41 specimen was limited, and the investigation of actual frost resistance was given
42 lower priority than the investigation of pressure related changes of the air void
43 structure. Therefore, the test area for the scaling test was only 8000 mm² per
44 specimen.
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53 **Results**

54 Though the triplet mixes of each dosage of air entraining agent in principle were
55 identical, they showed some variability. For example for the low dosage, the total
56 air content in fresh concrete varied from 3.3-5.7%. Results from air void analysis
57 are available for each specimen exposed to freeze/thaw testing. Therefore, results
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1 are here treated separately for each specimen, not as an average of 3 specimens
2 with the same dosage of air entraining agent. As a consequence, the test area for
3 the scaling test is relatively small, only about one tenth of the area prescribed in
4 the test standard. The uncertainty of the results is therefore larger than what can
5 normally be expected when using this standard.
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10 Mixes were prepared with either a high or a low dosage of air entraining agent.
11 For specimens with a low dosage of air entrainment, results are shown in Fig. 4.
12 Specimens with a high dosage of air entraining agent all had spacing factors lower
13 than 0.20 mm. This in combination with the low w/c resulted in very good frost
14 resistance. These specimens showed virtually no scaling, making the results less
15 useful for analysis as no difference in frost resistance can be detected despite
16 differences in air void structure. Therefore these results are omitted here.
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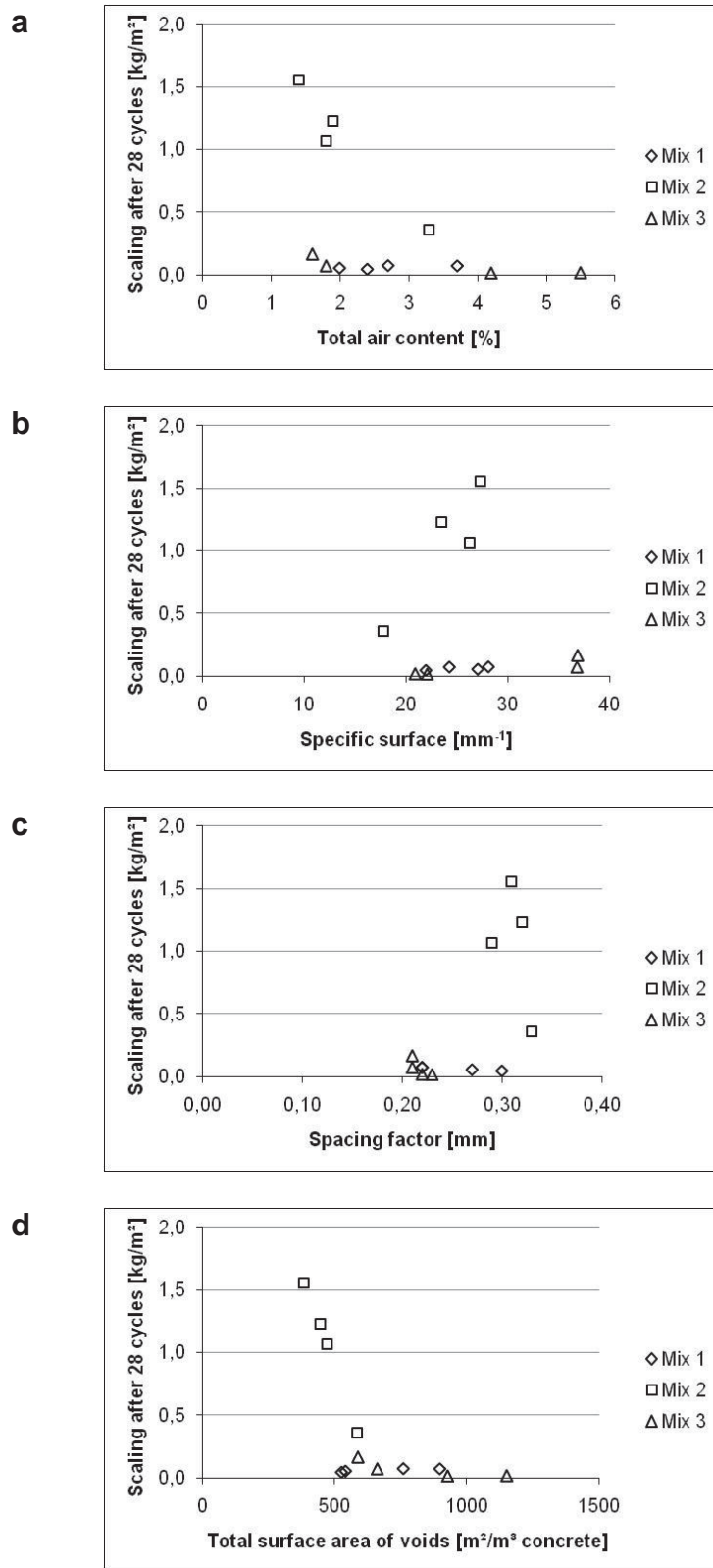


Fig. 4 Salt frost scaling as function of (a) total air content, (b) specific surface, (c) spacing factor, and (d) total surface area of air voids. Data are from Jensen (2005). Mix 1, 2, and 3 denote different mixes with same dosage of air entraining agent. For each mix, the resulting air void structure varies due to different external pressure applied during early hydration.

1 The results in Fig. 4 draw the same picture as is seen in previous sections: Neither
2 total air content or specific surface can be used as sole evaluation criterion, see
3 Fig. 4a and 4b. The same total air content or specific surface can result in very
4 different scaling. For the spacing factor, the results in Fig. 4c hint to a trend line
5 (the higher the spacing factor, the more scaling can be expected). However, the
6 total area of air voids is the parameter, which seems to give the best correlation to
7 salt frost scaling resistance. In Fig. 4d all 12 points look like they can be part of
8 the same curve, and the 4 points of mix 2 appear in a consistent way, which is not
9 the case in Fig. 4c.
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19 **3.5 Summary**

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21 When evaluating different characteristics of the air void system and their relation
22 to results of a salt frost scaling test, this is done in a purely qualitative way (which
23 curve looks “the best”), as no theory predicts the shape of the curve. However, all
24 4 laboratory studies depict the same tendency: when trying to describe the air void
25 system of concrete with only one parameter and linking this parameter to salt frost
26 scaling resistance, then the parameter of total surface area of air voids is as good
27 or superior to the well-known spacing factor (which again performs better than
28 specific surface and total air content). It is most obvious in the studies by
29 Backstrom et al. (1958b) and Jensen (2005), whereas the difference is marginal in
30 the studies by Siebel (1989) and Petersson (1989). The difference between
31 spacing factor and total surface area is especially distinct when comparing results
32 from concrete, where the amount of surface scaling is high.
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47 **4. Discussion**

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49 The assumption that frost resistance including resistance to salt frost scaling is
50 related to Powers’ spacing factor has been accepted as a premise in concrete
51 technology for more than 50 years. Alternative parameters have been suggested,
52 for example:
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- Philleo factor (Philleo 1983)
- Mean spacing (Attiogbe 1993)
- Flow length (Pleau and Pigeon 1996)

However, all the above mentioned alternatives focus on distance to nearest air void, so basically they follow the same tradition as Powers. Compared to this, using total surface area of air voids as evaluation criterion is fundamentally different.

4.1 Validity of observation

The method applied in this paper is inductive. The inductive proof is based on a number of observations. The proof becomes more convincing, the higher the number of observations pointing in the same direction, but there is always the possibility that a new observation will contradict the conclusion. It is therefore relevant to reflect on if the number of observations is sufficient to reach a trustworthy conclusion.

4 studies is not a very large number of observations for an inductive proof. However, the conclusion that salt frost scaling depends more on total surface area than on the spacing factor seems to be fairly robust. The pattern is consistent in all 4 studies, which have been performed on different types of concrete (e.g. w/c from 0.35-0.50) and with different test standards (different temperature cycles and different ways of registering scaling).

In concrete production, the air void system is normally established by a chemical air entraining agent, which stabilises air voids in the fresh concrete. However, for research purposes aimed at linking characteristics of air void structure to frost resistance, air entraining agents imply some difficulties. When the dosage of air entraining agent is increased, it influences both the number of air voids and their size: when the dosage is increased, it generally increases total air content and specific surface of the air voids, whereas it decreases the spacing factor. Like this, total air content, specific surface of air voids, and spacing factor become coupled variables, and it is not possible to vary only one and keep the other constant.

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2 Therefore it is hard to evaluate which parameter has the most significant effect on
3 frost resistance.
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5 In the 4 presented studies, the air void parameters are not coupled in the same way
6 as when only varying the dosage of air entraining agent. It is also varied by
7 applying different compaction regimes, by applying pressure, and by letting the
8 air entraining agent interact with other chemical admixtures. This increases the
9 likelihood that the total surface area is actually the decisive parameter, and not
10 just a secondary effect of the dosage of air entraining agent or another parameter
11 that is the real decisive parameter.
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20 All this indicates that the finding of the present investigation has general validity
21 for salt frost scaling, though the number of observations is only 4. However, more
22 experimental evidence will of course strengthen confidence in the conclusion. At
23 present, it is a preliminary conclusion, and more research is needed, before a final
24 conclusion can be drawn on if total surface area of air voids should replace the
25 spacing factor as evaluation criterion. In our laboratory at Technical University of
26 Denmark, we intend to launch a research project, which can provide more
27 experimental data.
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37 **4.2 Explanation for the findings**

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39 As explained in section 1, the preferred work method of engineers is a deductive
40 method. One of the advantages of using a deductive method is that it has its
41 starting point in a hypothesis or causal relation, and therefore it also has a built-in
42 explanation for what is observed. This is not the case when applying inductive
43 methods. In the present case, there seems to be a relation between salt frost
44 scaling and total surface area of air voids, but the study itself gives no explanation
45 why this may be the case.
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56 *4.2.1 A possible mathematical explanation*

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58 The total air content and the specific surface, measured by modified point
59 counting or chord counting, are exact physical characteristics of the air void
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1 system in hardened concrete. Therefore their product, the total surface area of air
2 voids, is also an exact measure. The spacing factor is not in the same way an exact
3 measure, it is an approximation to describe the distance to a free surface.
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7 For the paste/air volume ratio $p/A < 4.342$, calculation of the spacing factor is
8 based on the total surface area, so when the total surface area increases, then the
9 distance to a free surface will decrease. However, when $p/A < 4.342$, the air
10 content is high, and normally it is not under this circumstance problems with frost
11 resistance are observed.
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18 For $p/A > 4.342$, where most frost problems are observed, calculation of the
19 spacing factor is based on the assumption that all air voids have the same size and
20 are placed like nodes in a 3D lattice. These assumptions are tricky. The specific
21 surface is used as input parameter for the calculation. In the real system, a few
22 large air voids will not change the distance to a free surface very much. But in the
23 calculation of the spacing factor, a few large air voids will lower the specific
24 surface and thereby increase the spacing factor substantially. Therefore, when
25 some points in the scaling versus spacing factor mapping in section 3.1-3.4 are
26 placed differently from what is expected (viz. higher scaling follows higher
27 spacing factor), it may be the presence of a few large air voids that makes the
28 calculation uncertain. It is not trivial that different concrete mixes with the same
29 spacing factor also have the same distance to a free surface. In fact, concrete
30 mixes with the same spacing factor may in reality present very different distances
31 to free surfaces, and therefore also show differences in frost resistance.
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45 The starting point of the work of Phillio (1983), Attiogbe (1993), and Pleau and
46 Pigeon (1996) is that Powers' spacing factor is a too rough estimate, and they
47 refine it in different ways. For example, Philleo assumes that the uniform sized air
48 voids are placed randomly, and the Philleo factor is a distance, where only a small
49 proportion of the cement paste (usually 10%) lies further away from the nearest
50 air void. And when calculating the flow length distribution, Pleau and Pigeon uses
51 the actual air void size distribution as measured by air void analysis, combined
52 with random placement. So if the problem in linking frost resistance to Powers'
53 spacing factor is due to insufficiencies in the mathematical formulation of
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1 distance to the nearest air void, this should be overcome by the flow length
2 concept. However, the flow length has not yet proven to be a better measure than
3 the spacing factor in predicting frost resistance from air void data. This indicates
4 that the reason why the total surface area of air voids performs better than the
5 spacing factor is not purely mathematical.
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10 11 12 *4.2.2 A physical explanation for the findings*

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14 Chatterji (1985) has proposed a theory, which points out total surface area of air
15 voids (product of air content and specific surface area) as a relevant parameter for
16 frost resistance: According to this theory, ice formation starts in the air voids, and
17 a layer of ice will form on the air void's surface. Ice formation attracts capillary
18 water to the ice layer, and less water will be left to form ice in the capillaries.
19 However, ice layers will also act as barriers between empty spaces and freezing
20 solution in capillaries. A big air void with large surface area can withdraw
21 relatively much liquid from capillaries, and the ice layer will still be thin and
22 weak, so if ice formation propagates to the capillaries and starts to build up
23 pressure, the thin ice layer will burst and relieve the capillaries. In a smaller air
24 void, less water will be removed from capillaries during formation of the ice
25 layer, and the ice layer will be thicker and stronger. Further freezing will take
26 place in the remaining liquid in capillaries, and the generated pressure here may
27 exceed strength of the pore walls, before it breaks the ice layer.
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42 Corr et al. (2002) have studied ice formation in entrained air voids in hardened
43 cement paste in the following way: They used small specimens (8 x 7 x 2 mm)
44 and froze sealed samples at -7°C for 24 h. Then samples were put in liquid
45 nitrogen. In this way all unfrozen liquid froze almost instantly, thereby
46 immobilizing water molecules. While maintaining the low temperature, specimens
47 were fractured to open up air voids, which were then studied in a low-temperature
48 scanning electron microscope (LTSEM)¹. The results of Corr et al. do not agree
49 with Chatterji's theory, as they show that ice forms in discrete crystals, not in
50 layers on the inner surface of air voids. Ice crystals in air voids were roughly 5-20
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60 ¹ Images similar to those presented in the paper can be found on the internet:
61 http://www.ce.berkeley.edu/~paulmont/ice_formation_LTSEM.htm
62 (link registered October 2012)
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1 μm in diameter. The larger crystals had a hemispherical shape, whereas the shape
2 of smaller crystals was more irregular. When heating samples under the
3 microscope, ice crystals disappeared. Every location of crystals in the frozen
4 picture corresponded to a shell discontinuity. The SEM photos alone could not
5 disclose the reason for the discontinuities. Corr et al. suggested that it was either a
6 location, where water could penetrate the air void shell from the bulk cement
7 paste or the outlet of a capillary pore.
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14 Detrimental ice formation happens in capillary pores, where pressure can build
15 up. This is true, no matter if the damaging mechanism is hydraulic pressure or
16 microscopic ice lens growth. For both theories it is not important, if a capillary
17 pore is close to an air void; the important issue is that the capillary pore is
18 connected to the air void, as transport only to a very limited degree takes place
19 through the solid gel phase. In the case of microscopic ice lens growth, ice
20 formation will take place in the air void without pressure build-up, being feed
21 from the capillary, rather than in the capillary pore, where it can generate
22 substantial pressure.
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33 One can imagine all capillary pores placed in an ordered way, where they
34 systematically reach out for the nearest air void, and where capillaries connected
35 to air voids radiate from the air void peripheries. In this system the probability
36 that a capillary pore is connected to an air void is closely related to the number of
37 air voids, and not very much to their size. However, this is not a realistic system.
38 Instead, the capillary pores are distributed totally at random in the cement paste.
39 When a capillary pore connects to an air void, it is because it happens to be
40 intersected by the air void surface. In this system of randomly placed capillary
41 pores, the probability that a capillary pore is connected to an air void is related to
42 the surface area of air voids, not to the number of air voids. This is illustrated in
43 Fig. 5.
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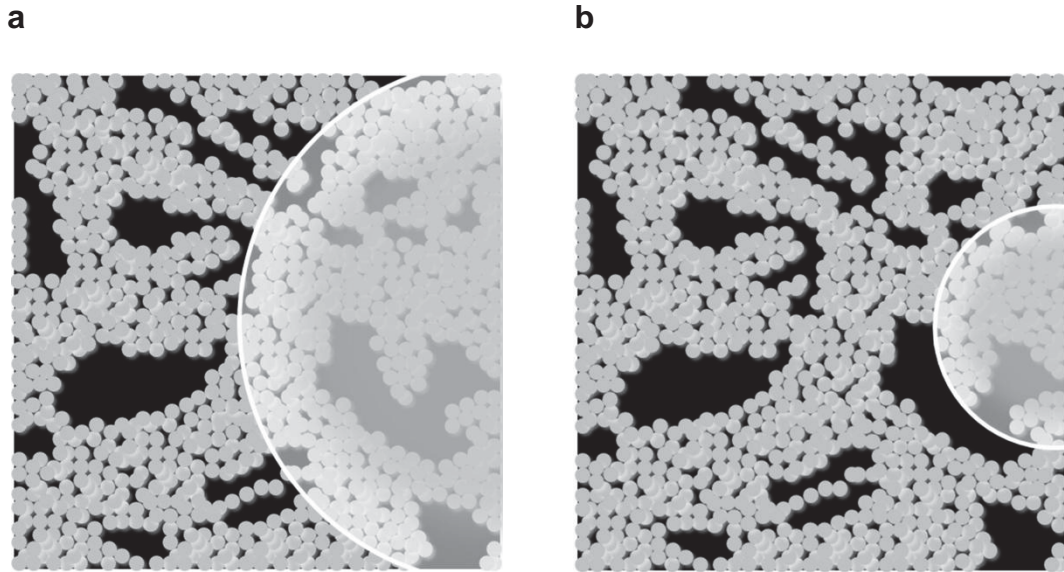


Fig. 5 Schematic models of paste structure (color definition: gel solid: grey; capillary pores: black; air void periphery: white rim). The structure of gel solid and winding capillary pores is identical for (a) and (b). The large air void in (a) intersects more capillaries than the relatively smaller air void in (b).

If the above explanation for the good correlation between salt frost scaling resistance and surface area of air voids holds, then it is more correct to use total surface area relative to paste volume as evaluation criterion than total surface area relative to concrete volume. However, it will only lead to minor changes of the trend shown in figures 1d, 2d, 3d and 4d, as within each of the 4 laboratory studies, the paste content is almost constant for all mixes.

It is also important to note that the relation between total surface area of air voids and probability that capillary pores are connected to air voids only is valid for spherical air voids. It is generally not true for air voids with more complex geometries. If one for example imagines that it is possible to create air voids with wrinkled surfaces instead of smooth surfaces, then the surface area of an air void can be varied by varying the wrinkle density and depth, without changing the likelihood that capillary pores in the vicinity will connect to it.

4.3 Total surface area of air voids and internal frost damage

In the presented investigation, focus has solely been on outer frost damage in the form of salt frost scaling. There has been no attempt to systematically investigate

if the total surface area of air voids also correlates better than the spacing factor to measures related to internal frost damage.

The look at just one study by Litvan (1983) indicates that the conclusion for internal damage may be the same: The study by Litvan and the study by Siebel (1989) have much in common, as the objective of both studies was to investigate how the presence of superplasticizers effects the frost resistance. Mortar specimens ($w/c = 0.65$) were prepared without superplasticizer and with different dosages of 3 commercial superplasticizers (A, B, and C). Each dosage of superplasticizer was tested with and without a fixed amount of air entraining agent. In total 16 different mortar mixes were prepared. For each mix, the air void structure in the hardened mortar was registered, and 2 specimens were tested according to ASTM C 666 (1977), procedure B, so specimens were frozen in air and thawed in water, and then the length change for each specimen was measured after 100 freeze/thaw cycles. Results are shown in Fig. 6.

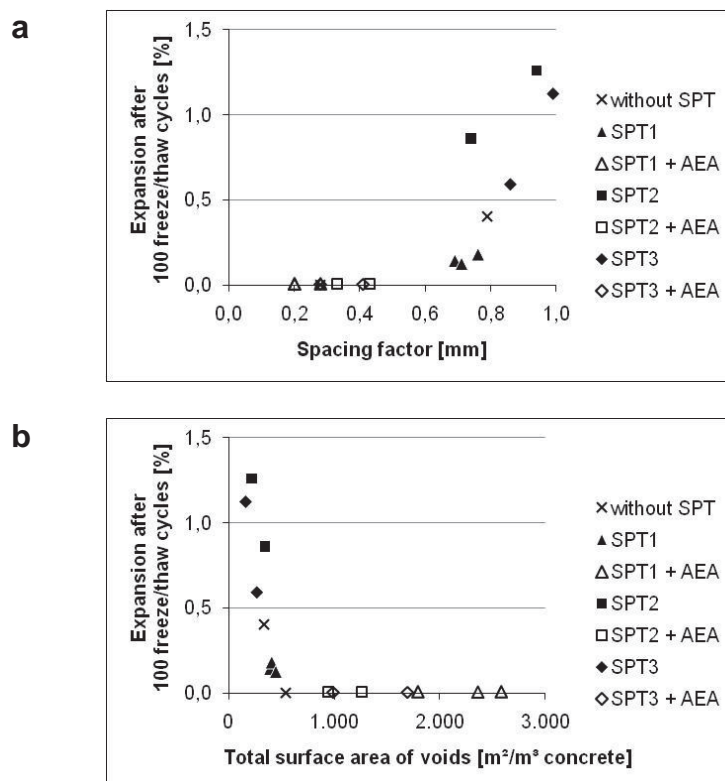


Fig. 6 Expansion during freeze/thaw action according to ASTM C 666 method B as function of (a) spacing factor, and (b) total surface area of air voids. Data were originally published by Litvan (1983).

1 Like for salt frost scaling, the relation between expansion and total surface area
2 seems to be more consistent than the relation between expansion and spacing
3 factor.
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7 The relation between internal frost damage and total surface area of air voids is
8 therefore also an obvious subject for further research.
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10 11 12 13 **5. Conclusion** 14

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17 4 studies on the relation between air void structure and salt frost scaling have been
18 reviewed. It is concluded that the total surface area of air voids is a better measure
19 than the well-known spacing factor, when characterizing the air void structures
20 ability to protect concrete against salt frost scaling.
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26 Mathematically, the spacing factor and the total surface area of air voids express
27 different things. The spacing factor expresses the likelihood that a capillary pore
28 is located in the vicinity of an air void. The total surface area expresses the
29 likelihood that the capillary pore is connected to an air void. This difference may
30 be the key to explain the finding of the review: In a capillary pore not connected
31 to an air void, ice formation can take place in the capillary, where it may result in
32 detrimental pressure. If the capillary pore is connected to an air void, ice
33 formation will instead take place in the air void, where it is feed by liquid from
34 the capillary pore, and in this way pressure build-up in the capillary pore is
35 mitigated. Like this, the decisive factor for salt frost scaling resistance, and
36 possibly also resistance to internal frost damage, is that capillary pores are
37 connected to air voids.
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48 49 50 51 **Acknowledgement** 52

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54 The work presented in this paper is made as part of a postdoc project on the relation between air
55 void structure and ice formation in concrete supported by the Larsen & Nielsen Foundation. This
56 support is greatly acknowledged.
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