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Freezing of air-entrained cement-based materials and specific actions of air-entraining agents

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Abstract

The freeze–thaw resistance of all cement-based materials is improved by incorporating a fine air bubble system in them. For acceptable life expectancy, incorporated air bubble volume should be about 25% of the cement paste. The specific surface of the air bubble system need to be above 25 mm^2/mm^3 and a spacing factor below about 0.16 mm. Powers explained these on the basis of his saturated flow hydraulic pressure mechanism. According to Powers' mechanism, the chemical nature of the air-entraining agent has no part in this improvement in performance.

Helmuth, one of the principal co-workers of Powers, has questioned a number of assumptions of Powers' mechanism. Most importantly, Helmuth showed that ice penetrates concrete as dendritic crystals. Furthermore, a number of workers have shown that the chemical nature of the air-entraining agent affects the freeze–thaw resistance of cement-based materials. Some air-entraining agents do not improve the freeze–thaw resistance even though they entrain air of the required characteristics.

In this paper, a modified and expanded version of Helmuth's model of ice penetration in concrete is utilised to explain the action of air bubbles. All air bubbles contain a layer of water on their inner surfaces. Surface tension spreads out water in the air bubbles as annular layers. Air-entraining agents may form or precipitate hydrophobic layers on air bubble surfaces. When an ice dendrite reaches an air bubble, the annular water layer freezes to an annular layer of ice. The hydrophobic layer on the air bubble surface reduces the ice–paste bond. Under this circumstance, the ice layer within the air bubble grows. During this growth, water is withdrawn from the surrounding by suction. A water movement under suction does not produce any expansive pressure. Withdrawal of water to the air bubbles explains the beneficial action of air entrainment. The specific efficiency of air-entraining agents is explained by the different degree of hydrophobicity produced by air-entraining agents.

Keywords: Degradation; Freezing and thawing; Air-entrained; Concrete; Agents; Spacing factor

1. Improvement of performance of cement-based materials due to air entrainment

All non-air-entrained cement-based materials deteriorate when exposed simultaneously to wet and sub-freezing conditions. In 1930s, it was observed that concrete made with cements from certain plants performed better in a freeze–thaw condition than concretes made with cements from other plants. Further studies of these concrete structures showed that the improvement was due to the incorporation of a finely dispersed air bubble system in those concretes. This incorporation of air bubbles was due to the use of some grinding aids during clinker milling. Air entrainment, though improves the performance of concrete, does not altogether stop concrete deterioration in a freeze–thaw environment. Subsequently a large volume of research was carried out to define the characteristics of entrained air bubble system for an acceptable concrete life span. The requirements are about 5–7% air by the volume of concrete and a minimum specific surface of 25 mm^2/mm^3 of air. Calculated on the volume of cement paste, i.e. volume of cement plus water, the required air content is about 25%.

2. Mechanism by which air entrainment improves the performance of cement-based materials in a freeze–thaw environment

Powers and his co-workers carried out extensive research on this aspect. Powers proposed that in an

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air-entrained concrete there are three classes of pores [1]. The first class consists of a system of very fine pores within the dense packing of cement hydration products. This class of pores is termed the gel pores. The radii of these pores are very small. Water present in this class of pores seldom freezes under usual freezing conditions of concrete use. The second class of pores is the remnant of the original water filled spaces of fresh concrete mix. This class of pores is termed the capillary pores. These pores are larger than the gel pores. Layers of cement hydration products with associated gel pores separate individual capillary pores from each other. The capillary pores are contiguous with the gel pores so that water can move in and out of the capillary pores with changes in the ambient conditions. Water present in the capillary pores freezes under usual freezing conditions of concrete use. Due to the size restriction, water present in a capillary pore freezes at a temperature lower than 0 °C. The smaller the capillary size the lower is the freezing temperature. In air-entrained paste or concrete, a third class of pore exists. These are mainly entrained air bubbles. The sizes of these air bubbles are very much larger than the other two classes of pores so that the surface of an air bubble could be treated as a flat surface. These air bubbles are supposed to be empty. Normally the capillary pores are separated from the air bubbles by layers of cement hydration products with associated gel pores.

Powers explained the beneficial effect of air entrainment by postulating that in a saturated concrete only capillary and gel pores are saturated. At any subfreezing temperature, homogeneous nucleation of ice occurs only in capillary pores of appropriate size. Once ice has formed in a saturated capillary pore, it contains more water than its volume can hold. This excess volume of water is forced out through the contiguous gel pores to the nearest empty air bubbles or to the outer surfaces of the sample. During this forcing of water a saturated flow hydraulic pressure develops on the surfaces of the flow channels. If this pressure is higher than the bursting strength of the sample then damage occurs. The magnitude of this hydraulic pressure depends on the rate of water flow i.e. the rate of ice formation; the distance between the capillary pore and the nearest escape surface; and the permeability of the gel pores. Powers developed Eq. (1) to calculate the hydraulic pressure development [2]

$$P = a\left(1.09 - \frac{1}{s}\right)\frac{uR}{\kappa}\left(\frac{L^3}{r_b} + \frac{3L^2}{2}\right), \qquad (1)$$

where P is the hydraulic pressure in Pascal, a is a factor, depending, among other things, on the viscosity of water (kg/m s), s is the saturation coefficient of the cement paste, u is the amount of water in kg per kg of cement, which freezes when the temperature falls by one degree (kg/kg °C), R is the rate of cooling in °C/s, κ is the specific or intrinsic permeability of the paste in m^2, r_b is the average radius of air bubbles in metres, and L is the shortest distance between two air bubbles, also known as the Powers spacing factor (m).

The sample deteriorates when P exceeds the bursting strength of the sample. More correctly, P should exceed the bursting strength of ice-strengthen sample [3].

Other things remaining constant, P decreases with decreasing L. This dependence on L explains the beneficial effect of air entrainment. Eq. (1) also says that L and κ are the important factors. For a concrete sample of a definite water/cement ratio κ is constant. Controllable factors are R, s and L. L is dependent on the volume of entrained air and its specific surface. An L value of 0.16 mm or lower is generally assumed to impart the required protection in a freeze–thaw environment. The chemical nature of the air-entraining agent does not affect the beneficial effect of the entrained air bubble system. The disrupting pressure, P, becomes appreciable when the saturation coefficient approaches 1. When the saturation coefficient, s, is lower than 0.917, P is negative and the sample is under tension. No disruptive pressure can develop if the water flow is unsaturated.

3. A critical evaluation of Powers saturated flow hydraulic pressure hypothesis

Helmuth, a co-worker of Powers, examined different assumptions of the saturated flow hydraulic pressure mechanism. In the following Helmuth's evaluation will be presented first with some additional comments. Subsequently evaluation of other workers will be presented.

(a) Helmuth found that the assumption of empty air bubbles is not valid. In virgin saturated pastes, on the average, about 36% of the entrained air voids are water filled within 24 h [4]. Warris also reported similar filling of air bubbles [5]. Warris reported that the degree of filling increases with the length of under-water storage. The surface tension spreads water in each air bubble to an annular layer on the surface. This is consistent with the petrographic examination of outdoor concrete. In these samples, most air bubbles have annular layers of ettringite or calcium hydroxide on their surfaces indicating the presence of annular water layers [6]. In homogeneous ice nucleation, as assumed by Powers, the initial ice nucleation should occur in these annular water layers. Ice nuclei in these annular water layers are free from all capillary size restrictions. Subsequent ice growth should form ice layers on the air bubble surfaces and effectively stop water flow to the air bubbles.

The above noted filling raises a fundamental question about the determination of 'spacing factor'. To evaluate the 'spacing factor' one has to measure air bubble characteristics i.e. volume and specific surface of the air voids.

This can only be done on a dry concrete specimen. This means that the measured parameters refer to the dried concrete and not to the wet concrete. Free air volume in wet concrete will definitely be less by the degree of filling. It is not obvious that this water filling will be uniform over all bubble sizes. The 'spacing factor' will increase by twice the thickness of the water layer on the bubble surface. These aspects seem to have gone unnoticed.

(b) Helmuth showed that ice nucleation does not occur homogeneously throughout the volume of a concrete [7]. Instead ice penetrates from outside as dendrites. Bager and Sellevold have also reported similar penetration of ice from outside [8]. This dendritic ice penetration is facilitated both by super-cooling of water and efficient ice–paste bond [3]. When ice dendrites reach air bubbles, the water layers within air bubbles form ice layers.

(c) Eq. (1) predicts that increasing rate of freezing, R, increases P. An increase in P leads to increased expansion of the sample. In contrast to the above expectation, Helmuth found that an increased rate of freezing decreases the expansion [9]. Helmuth explained this anomaly as due to a transfer of capillary water to gel with lowering temperature. There are other contributory factors to a lowered rate of expansion at increased rate of freezing. An increased rate of freezing means that the outer volume of the sample is at a lower temperature than would be at slower rate of cooling. This outer volume is also filled with ice. Ice contracts at sub-zero temperatures and compresses the sample [3,10]. Furthermore, the strength of the ice filled zone increases with lowering temperature [3,10]. This compression and increased strength reduce any possible expansion due to further freezing.

(d) Helmuth observed that freezing might damage even self-desiccated pastes with unsaturated capillary pores [9]. Among others, Whiteside and Sweet also reported similar observations [11]. This means that for a damage to occur capillary and gel need not have to be saturated from the start.

From his extensive results Helmuth concluded, "the expansion-producing mechanism in moist, hardened paste, both with and without entrained air, is not the development of pressure in the water in all the pores, ..." [9]. Helmuth further concluded " This must mean that in the tests of pastes containing entrained air, unsaturated (water) flow to air voids occurred early enough and to such an extent that positive pressures and saturated flow did not develop" [9]. However, Helmuth did not explain why the water flows to air bubbles failed to develop positive pressure. Helmuth's results led to the retraction of Powers' saturated flow hydraulic pressure mechanism. In spite of this retraction, Powers' hypothesis remains the most referred mechanism.

(e) Discussions with researchers, on the both sides of Atlantic, revealed that the non-physical nature of the 'spacing factor' has not been fully appreciated. To estimate the 'spacing factor' the number of air bubbles per unit volume of concrete is first calculated from the measured entrained air volume and its specific surface. Thus, the air bubbles become of equal size. The bubbles are assumed to be distributed on a cubic lattice points. From this distribution, the 'spacing factor' is calculated. None of the above two assumptions is realistic and achievable in practice. 'Spacing factor' is thus not a physical quantity but a mathematical construct. It also hides all the effects of bubble size distribution. Powers was fully aware of this artificial nature. Even with a cubic distribution, a different bubble size distribution, keeping the specific surface constant, gives a different 'spacing factor' [12]. Fig. D of Powers' 1954 paper shows that concrete samples having the same 'spacing factor' and tested in the same laboratory can have quite different freeze–thaw resistance although there is a strong trend of improved performance with decreased 'spacing factor' [13]. These results were obtained at Portland Cement Association and US Bureau of Reclamation. These results show that 'spacing factor' is not the sole determining factor; other factor(s) is also working.

(f) Another unexplained aspect is the specific effect of an air-entraining agent. The degree of improvement in the performance of an air-entrained concrete depends on the chemical nature of an air-entraining agent [14,15]. Mielenz, who was the Research Director of Master Builder at the time, evaluated performances of different air-entraining agents on concrete samples with matched composition, volume of entrained air and calculated spacing factor. Mielenz found differences among different agents [14]. Chatterji was aware of the non-physical nature of the 'spacing factor' and that it conceals the effects of bubble size distribution [12]. Chatterji therefore evaluated performances of different air-entraining agents using cylindrical samples from a single batch of hydrothermally produced industrial aerated product. The air void and material characteristics remained invariant throughout the series. The only variable studied was different air-entraining agents. Chatterji found differences among different air-entraining agents [15]. Recently Edmeads and Hewlett compared performances of four types of air-entraining agents in concrete samples containing about 5% air [16]. Table 1 shows the grading of Edmeads and Hewlett. From Table 1 it is obvious that sodium oleate performs better than other agents. The performance of phenol ethoxylate is no better that non-air-entrained concrete in spite of entraining about 5% air. One would expect that Edmeads and Hewlett were aware of 'spacing factor' and taken care of that though they have not mentioned it in the book. Thus, all the above workers independently came to the same conclusion that different agents perform differently. In this connection, it is of interest to note that an external

Table 1
Performance of different air-entraining agents in air-entrained concrete

Agent	Air content (%)	Rating
Sodium oleate	5.6	86
Vinsol	5.2	57
Sodium lauryl sulphate	5.8	46
Phenol ethoxylate	5.2	7
Reference	2.0	5

application of sulphate liquor, a known interfacial active agent, reduces frost heaving in soils [17].

This specific effect was also noted in ASTM C233 and C260 specifications. These specifications require that performances of all air-entraining agents should be compared against that of vinsol resin. Any agent that performs less than 80% that of vinsol should be rejected [18,19]. This statement acknowledges that all air-entraining agents are not equally effective. Phenol ethoxylate is the extreme case of poor performance. Powers' hypothesis does not place any importance to the chemical nature of the air-entraining agents.

With the retraction of Powers' hypothesis, the beneficial action of air-entrainment becomes unexplained. The specific efficiency of air-entraining agents is also unexplained. In this paper, I shall modify and extend Helmuth's model of ice penetration to explain both the above effects. I shall also show why the 'spacing factor', in spite of its non-physical nature, is so successful. However, first a discussion of the nature of air-entraining agents is in order.

4. The nature of air-entraining agents

The air-entraining agents may be classified into two general types. One type reacts with calcium hydroxide solution of cement paste to precipitate insoluble calcium salt. This type includes vinsol resin, sodium adipate, sodium oleate etc. With this type, the surface tension of water is not reduced. These calcium salts are hydrophobic. Collection of these hydrophobic salts at the water–air–cement grain contact regions is the main cause of both air entrainment and bubble stability [20]. In hardened concrete, these calcium salts remain on the surface of the air bubbles. In all his work, Helmuth used vinsol resin; even then, he found that 36% of the air voids are filled with water. This shows that in spite of the surface coating by water repellent calcium salts water enters the bubble volume.

The synthetic tensides (surfactants) form the second type. These consist of chains of aliphatic and/or aromatic hydrocarbons with a water-soluble group like SO_4 or SO_3 or OH etc. attached at one end. Calcium salts of this group, when formed, are water soluble. The solubility behaviour of tensides in water is anomalous. Some tensides have a critical temperature, called Krafft point, below which their solubility drops very sharply. Reported data show that the solubility of sodium decylsulphonate in water at 0 °C is about 0.01 $\mathrm{mol\,dm^{-3}}$ whereas above 25 °C it is highly soluble. Suppliers of synthetic air-entraining agents are aware of this phase separation and recommend that agents should be stored above a critical temperature. On the other hand, the solubility of dodecylhexaoxyethylene glycol monoether at 0 °C is about 38% by weight [21]. All tensides lower the surface tension by preferentially collecting at the air–water interface. This lowering of surface tension is the main cause of both air entrainment and bubble stability. In hardened concrete, the surfaces of air bubbles have higher concentration of these tensides than within the paste.

5. Freezing of air-entrained cement-based materials

Consider an air-entrained concrete in an outdoor environment. In colder climates, wet autumn normally precedes freezing winter. During autumn, the concrete sample gradually cools and at the same time absorbs water from rain. During cooling, the pressure within the air bubbles drops and water, from the surrounding saturated paste, enters the air bubbles. Between 4 and 0 °C, water within a saturated paste expands and a part of water is pressed into the air bubbles [3,10]. The last two water movements are in addition to that observed by Helmuth and Warris and occur irrespective of any other processes. Thus near the freezing point air bubbles always contain water layers on their surfaces. This water also carries with it tensides used to incorporate air bubbles. If the tensides used have Krafft points above 0 °C then they separate out of solution. During this separation, the organic parts of these tensides attach themselves to cement grains by a process similar to that of superplasticizers. This means that they remain on the surfaces of the air bubbles. This also means that at 0 °C the surfaces of the air bubbles are either covered with a layer of hydrophobic calcium salts or tenside separated from solution or an enriched tenside solution.

Freezing normally starts at the outer surfaces where temperature is lower than within concrete. External ice and snow nucleate ice formation within concrete. Helmuth and Bager and Sellevold have shown that ice penetrates the concrete as dendrites. Supercooling and ice–cement bond are the two processes involved in this dendritic ice penetration in concrete [3]. For large concrete samples supercooling seldom exceeds −2 to −4 °C. When an ice dendrite reaches an air bubble, the annular water layer at the bubble surface quickly forms an ice layer. Due to the absence of any capillary-size restriction the annular water layer behaves like bulk water and freezes quickly at about 0 °C. This annular ice layer is directly in contact with either a thin precipitated layer or with cement pastes itself. The thin precipitated layer can either be hydrophobic calcium salt like calcium oleate or phase separated tenside like sodium decylsulphonate. The thin precipitated layer in its turn is in contact with a saturated cement paste. If the tenside used does not separate out at 0 °C like dodecylhexaoxyethylene glycol monoether solution then ice is in direct contact with cement paste.

On further cooling, an annular ice layer may either grow within the air bubble drawing water from the surrounding paste or act as a source of further dendritic penetration into the paste. Interestingly Powers was aware of the beneficial effect of this process of "extraction of water from gel by ice crystals in air voids" [13]. The choice depends on Laplace–Dupree equation (2) [3]

$$\Delta p_{\mathrm{i}} + \Delta p_{\mathrm{w}} = \frac{2\gamma_{\mathrm{iw}}}{r_{\mathrm{i}}}, \tag{2}$$

where Δp_{i} is the restraining pressure acting on the ice crystal and Δp_{w} is the suction pressure in water. The direction of suction is away from the ice crystal. γ_{iw} is the ice–water interfacial tension at the relevant temperature. r_{i} is the radius of the ice–water interface.

In the present context, r_{i} is the radius of either a capillary pore or a gel pore. In the absence of both Δp_{i} and Δp_{w} the ice layer cannot penetrate very narrow gel or capillary pores of radius r_{i}. Ice grows within the air bubble drawing water from the surrounding [3]. In a saturated paste, Δp_{w} is non-existent at least at the initial stage of freezing. In the present context the restraining pressure on ice, Δp_{i}, is mainly the ice–substrate bond. For any given r_{i} there is critical Δp_{i} below which ice will not penetrate into the paste. To go any further the ice–substrate bond strength has to be evaluated.

Ice is a strong material and its bond with hydrophilic materials like hardened cement or glass is nearly as high as its shear strength. Difficulty experienced in removing a compacted ice layer from concrete pavement is an example of high ice–concrete bond. Ice–substrate bond with hydrophobic materials is lower than hydrophilic materials. Attention to extensive literature on above aspects has already been drawn in earlier papers [3,10]. The magnitude of lowering of ice–hydrophobic substrate bond depends on the nature of the substrate surface. When the ice layer is in direct contact with a layer of hydrophobic calcium salt then the ice–hydrophobic layer bond decreases with the degree of hydrophobic nature of the layer. This explains the difference in performance between vinsol resin and sodium oleate [16]. When the ice layer is in direct contact with a layer of phase separated tenside the ice–substrate bond will not be as low as that between ice and hydrophobic substrate. Sodium lauryl sulphate belongs to this group. When no phase separation occurs then ice–cement paste bond is similar to that between ice and cement paste in absence of any air-entraining agent. Phenol ethoxylate belongs to the last group.

It means that the type of air-entraining agent, used to incorporate entrained air, alters Δp_{i}. However, ice–substrate bond strength is always finite and positive. When Δp_{i} is low the annular ice layer does not penetrate the surrounding paste but grows within the air void by drawing water from the surrounding gel or capillary pores. The growth of annular ice layer is inversely related to Δp_{i}. Eq. (2) shows that this water flow toward the ice crystals has the character of suction towards the ice layer. The associated hydraulic pressure is always subatmospheric and cannot cause any damage to the paste. This transfer of water from paste to air bubbles, under suction, explains the beneficial effects of air bubbles. This also explains Helmuth's comments "This must mean that in the tests of pastes containing entrained air, unsaturated (water) flow to air voids occurred early enough and to such an extent that positive pressures and saturated flow did not develop" [9]. This alteration of Δp_{i} explains both the absence of positive pressure generation as well as the specific efficiency of an air-entraining agent. An agent, which does not change Δp_{i} compared to water does not improve freeze–thaw resistance of a concrete. Phenol ethoxylate belongs to this group.

The growth of the annular ice layer progressively compresses the entrapped air in the air bubbles and raises the air pressure. Ultimately the combination of the ice–paste bond and the air pressure becomes high enough to stop the growth of the annular ice layer and begin dendritic ice penetration in the paste. From this stage onward an air-entrained concrete behaves as a non-air-entrained concrete. On further cooling ice dendrites penetrate cement paste. This ice penetration has two effects. It increases the depth of high strength, ice-filled part of concrete and at the same time increases the hydrostatic pressure in still unfrozen water. The hydrostatic pressure development and enhanced strength of ice-filled concrete have been discussed in earlier papers [3,10]. If at this stage the volume of unfrozen water is sufficiently large, the hydrostatic pressure could be high enough to cause damage to concrete. In this context, the process of thawing is also important [22]. Normally thaw starts from the exposed surfaces of the specimen. Very often thaw occurs during rain or water condensation. As thaw proceeds inward, melting of ice within the specimen creates suction and rain or condensed water penetrates the specimen. This water ingress saturates gel and capillary pores. This newly penetrated water hinders thawed water in air pores to re-enter the paste. If this freezing–thawing cycle is repeated without any dry spell in between then some of the air bubbles, especially those near the exposed surfaces, get water filled. Water filled air bubbles cannot draw water from the paste during freezing. Moreover, it adds to stills unfrozen water where hydrostatic pressure develops and thereby accelerates the damage.

The development of hydrostatic pressure in still unfrozen water does not depend on the overall degree of saturation of concrete specimen. A volume of water which is isolated by ice jacket from its surrounding is capable of developing this hydrostatic pressure even if the surrounding space is air. The process has been discussed and evidence produced in an earlier paper [10]. This explains why an unsaturated concrete or even those self-desiccated, under appropriate condition, can be damaged.

This modified Helmuth model shares a characteristic with Powers' saturated flow hydraulic pressure mechanism. In both these mechanisms, air bubbles provide space for excess water to escape. In Powers' model water from capillary pores is forced through the gel pores to the air bubbles developing a destructive pressure. In the present model water is sucked to the air bubbles by ice already present in them and as a result no destructive pressure develops. This statement follows directly from Hagen–Poiseuille equation. In the case of forcing water through a saturated capillary, the pressure differential is positive and the pressure on the capillary wall is positive. In Powers theory excess water is produced at the site of ice formation within the capillaries and then forced through the gel pores to the empty air voids which are at atmospheric pressure so the pressure differential is positive and the pressure on the walls of the gel pores is also expansive. In the case of suction, the pressure differential is negative water being at the atmospheric pressure. This is equivalent to the process of "extraction of water from gel by ice crystals in air voids." In this case, there is no expansive force on the walls of the gel pores.

There is a widespread view that all types of fluid flow through a capillary cause positive pressure development on the capillary wall. This can easily be shown to be untrue by connecting soft, thin walled rubber tubing to a vacuum pump. In this case, the maximum flow is determined by the carrying capacity of the tube. If this volume flow is lower than the pump capacity, the tube wall collapses. On the other hand, if the tubing is connected to a powerful blower then the diameter of the tube easily expands even though the other end is unobstructed.

The above mechanism also explains the apparent success of 'spacing factor'. It has to be noted that, for any given air-entraining agent, the thickness of the ice layer on the surfaces of the bubble system, which stops further water ingress is fixed. The maximum amount of water that can flow to the bubble system, from the paste, is proportional to the total surface area of the entrained air bubble system. Higher the amount of water removed from the paste better will be its performance. For a given air-entraining agent higher the total surface area of the air bubble system more water is drawn to the bubbles and better is the concrete performance. The 'spacing factor,' by definition, is inversely related to the total air surface area. The higher the total surface of air bubbles per unit volume of concrete the lower is the 'spacing factor' and better is the concrete performance in a freeze–thaw environment. This explains the apparent success of 'spacing factor' in spite of its non-physical construction. However, the relationship is not one to one due to the mathematical construction of 'spacing factor' and its measurement technique. In recent years this has reflected in various national requirement on the determination of the 'spacing factor' i.e. the stipulation that cord size of the pores should be measured within a specified lower and upper bounds.

Acknowledgements

In early summer Lars Romben, Eva Bergman and I planted some seeds in the woods surrounding the Swedish Cement and Concrete Research Institute, Stockholm. Those are now germinating in late autumn. Will they survive the coming winter years! I wonder.

I could not deny the wishes of my daughter Ena and my brother Malay by not writing this paper.

References

[1] Powers TC, Helmuth RA. Theory of volume changes in hardened Portland cement pastes during freezing. Proc Highway Research Board 1953;32:285–97.

[2] Powers TC. The air requirement of frost-resistant concrete. Proc Highway Research Board 1949;29:184–202.

[3] Chatterji S. Aspects of freezing process in porous material–water system. Part 2. Freezing and properties of frozen porous materials. Cem Concr Res 1999;29:781–4.

[4] Helmuth RA. Dimensional changes of hardened Portland cement pastes caused by temperature changes. Proc Highway Research Board 1961;40:315–36.

[5] Warris B. The influence of air-entrainment on the frost-resistance of concrete. In: Proceeding No. 36, Swedish Cement and Concrete Research Institute, Stockholm, 1964.

[6] Chatterji S, Christensen P, Thaulow N, Jensen AD, Gudmundsson H. Filling up of pores and fractures in weathered concrete structures. In: Proceedings of the 3rd International Conference on Cement Microscopy, Texas, 1991. p. 298–306.

[7] Helmuth RA. Capillary size restriction on ice formation in hardened Portland cement pastes. In: Proceedings of the IV International Symposium on Chemistry of Cement, Washington DC, vol. II. 1960. p. 855–69.

[8] Bager DH, Sellevold EJ. Ice formation in hardened cement paste. Part II—Drying and resaturation on room temperature cured pastes. Cem Concr Res 1986;16:835–44.

[9] Helmuth RA. Discussion of the paper "Frost action in concrete." by P. Nerenst. In: Proceedings of the IV International Symposium on Chemistry of Cement, Washington DC, vol. II. 1960. p. 829–33.

[10] Chatterji S. Aspects of freezing process in porous material–water system. Part 1. Freezing and properties of water and ice. Cem Concr Res 1999;29:627–30.

[11] Whiteside TM, Sweet HS. Effect of mortar saturation in concrete freezing and thawing tests. Proc Highway Research Board 1950;30:204–16.

[12] Chatterji S. The spacing factor in entrained air-bubbles. Has it any significance? Cem Concr Res 1984;14:757–8.

[13] Powers TC. Void spacing as a basis for producing air-entrained concrete. Bull Portland Cement Assoc, Chicago 1954;49A.

[14] Mielenz RC. Use of surface-active agents in concrete. In: Proceedings of the V International Symposium on Chemistry of Cement, Tokyo, Part IV. 1968. p. 1–102.

[15] Chatterji S. Freezing of aqueous solutions in a porous medium. Part 1. Cem Concr Res 1985;15:13–20.

[16] Edmeades RM, Hewlett PC. Cement admixtures. In: Hewlett PC, editor. Lea's chemistry of cement and concrete, 4th ed. London: Arnold; 1998. p. 842.

[17] Penner E, Robillard P. The use of sulphate liquor to reduce frost heaving in soils. Engrs Inst Canada, Ottawa, Trans 1959;3:107–9.

[18] ASTM C-233. Air-entraining admixtures for concrete. American Society for Testing Materials, 1916 Race St., PA 19103.

[19] ASTM C-260. Standard specification for air-entraining admixtures for concrete. American Society for Testing Materials, 1916 Race St., PA 19103.

[20] Friberg S. Emulsion stability. In: Friberg S, editor. Food emulsions. New York: Marcel Dekker; 1976. p. 1–38.

[21] Ottewill RB. In: Tadros ThF, editor. Introduction Surfactants. London: Academic Press; 1984. p. 1–18.

[22] Chatterji S, Jensen AD, Thaulow N, Christensen P. Freezing of aqueous solutions in a porous medium. Part 2. Freezing of mixed solutions of air-entraining agents and water reducers. Cem Concr Res 1985;15:729–33.