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Review

Review on the modelling methods for the frost action characterization in cementitious materials at different scales

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Abstract: Experimental studies on the frost action in concrete have showed a complex behaviour due to a high thermo-hydro-chemo-mechanical coupling. Many researchers have developed models to simulate freeze–thaw effects in cementitious materials. They showed the difficulties to take into account all phenomena: hydraulic, hydrostatic and osmotic pressures into pores; swelling and shrinkage; scaling, etc. Some researchers have firstly proposed descriptive models with the objective to reproduce the macroscopic observations, by calibrating the behaviour law and to show the influence of each parameters. Other researchers have proposed predictive models without calibration but with probabilistic methods. The different models show interesting results but are limited to few physical phenomena listed above. This paper presents a review on these different modelling methods and the limitations of each model. A short discussion is given to suggest a coupling method to consider all physical phenomena.

Keywords: predictive models; descriptive models; cementitious materials; freeze–thaw cycles; poro-mechanics

1. Introduction

This paper aims to present a review on the different modelling methods for the analysis of the frost action, particularly the freeze–thaw effects, on cementitious materials. The power of the freezing water can not be underestimated in cementitious materials [1–3]. Citing the experiment of Hyugens (1667) who has frozen water in two portions of welded cannons and observed for the first portion a breakthrough in the iron due to an explosion and for the other portion, the formation of ice filaments outgoing microscopic holes at the location of the welds. At a smaller scale, the cannons portions could be considered like pores in a porous medium.

At low temperatures, the pore water in cementitious materials transforms in ice. The experimental work of Gold (1958) [4] showed that when ice is constrained at temperatures from −3 to −40 °C, it has a perfectly elastic behaviour as the applied stress remains below a certain value and for a quite short time stress. For temperatures between 0 and −40 °C, the Young's modulus and the Poisson's ratio of ice can be considered constants with the respective values of 8.34 GPa and 0.35. In a porous medium, the thermal expansion of ice [4] at low temperatures leads to deformation in pores and differential dilation between ice and the solid skeleton. So the frost behaviour of concrete is controlled by its porosity. Two types of porosity can be distinguished: porosity of cement hydration products, capillary porosity which are residual spaces not through by hydration products [2]. The cement paste's hydration products can be considered as porous gels surrounding the non-hydrated clinker and some non colloidal hydrates, as the calcium hydroxide (CH).

When the smallest particles of the cement paste are dried, they shrink permanently and irreversibly. This shrinkage is so significant that a cement paste with a water-to-cement (w/c) ratio equal to 0.5 may reabsorb only 95% of the water volume it was initially able to contain. The partial vacuum of the capillary pores during hydration is a very important factor which contributes to the frost resistance of concrete. If the capillary space is filled with liquid water at least 91.7%, then it will be completely saturated with liquid water and ice after freezing if we consider an increase of 9% of the water volume. The experiments of Powers [5] showed that concrete having an initial water saturation degree more than 91.7% are not able to resist to pressures generated during freeze–thaw cycles.

During the ice nucleation in fine capillary pores of the cement paste, the water movement and the growth of the ice front generate pressures on the capillary pores walls which lead to the deformation of the cement paste. Concrete is thus not extensible enough to accommodate deformations to resist to such pressures. Pressures generated on pores walls mainly depend on the permeability of the material, that can let water in excess to escape from the saturated area. In addition, ice tends to push the water from the gel pores to capillary pores which are connected [6]. A hydraulic pressure is generated to resist to this flow. Powers [6] has showed the influence of air bubbles in the cement paste subjected to frost actions. These experiments allowed assessing the hydraulic pressure exerted by ice close to these bubbles. Powers has explained that the air bubbles play an important role by receiving the expelled liquid water. He has calculated the critical distance between the pore and the air bubble ($L = r_m - r_b$, where r_b is the pore radius and r_m the radius of the sphere influence for which the water flow is not critical). Later, Litvan [7] has given an another explanation for the water movement during freezing. In a cement sample saturated with liquid water and exposed to a temperature of about −1 °C, liquid water in the cement paste and ice crystals on the sample boundaries are simultaneously present. However, the non-frozen water has a vapor pressure higher than that of the ice and the phase equilibrium can not be maintained without violating the fundamental laws of Nature.

As this vapor pressure difference can not be changed by the solidification of water, then the balance will be reached by another process. It is by adjusting the amount of liquid water in the cement paste (at a relative humidity less than 100%). Liquid water is expelled from the cement paste in order to maintain the reference relative humidity of the material. Therefore, this expelled liquid water freezes on contact with the frost air in the external environment and ice accumulates on the surface of the cement paste. Then, the partially dried cement paste will be in equilibrium with the external ice. When the temperature decreases this process will start again and the cement paste will continue to dry. These phenomena result in damage of concrete in most cases. Indeed, the liquid water contained in the ‘healthy’ concrete is pushed into the existing cracks and this water may solidifies by generating pressures. This mechanism is important if the water expulsion and freezing are fast. The porous structure of the cement paste is therefore a relevant factor for its durability.

Various studies have focused on the evolution of deformation at low temperatures. The decrease of strains describes a drying effect of the material, explained by an osmotic effect which leads to a decrease of the liquid water volume in the finest pores, or because ice shrinks at low temperatures [8]. During the phase change from water to ice, deformations increase under the effect of the pressure variation in pores. In some cases, deformations are starting to decrease after the frost “peak” indicating drying of the material. In other situations, deformations continue to grow after the frost “peak”, leading to the swelling of the material. The behaviour of cement pastes at low temperatures may gives an indication of the behaviour of concrete under the same conditions. The main porosity of concrete is essentially in the cement paste. But the pores of the concrete aggregates can also affect the frost resistance of concrete as we shall see. Thermodynamic and chemical considerations also help to highlight other pressures into concrete. All of these theories is recalled in [9]. Indeed, the pores cementitious materials do not contain pure water but have a certain chloride concentration (or other chemical ions), as in the transition from water to ice, changes in solute concentration are the cause of the emergence of an osmotic pressure [10, 11].

However, none of these theories alone explains the experimental observations made on concrete subjected to freeze–thaw cycles. Indeed, many experimental studies on cementitious materials subjected to freeze–thaw cycles showed that degradation or failure of the sample could not be predicted with theoretical laws as the degradation time varied [12, 13]. In addition, these studies showed the great disparity in results depending on the type of cement, type of aggregate [14, 15], the w/c ratio [16–20] and the amount of cementitious binder [21, 22]. So, it justifies the need for numerical models to predict this behaviour. Many researchers have developed models to simulate the behaviour of cementitious materials submitted to freeze–thaw cycles.

This paper presents a stat-of-art of different modelling methods, distinguished in two approaches:

- The description of mechanical, thermodynamic and/or hydraulic phenomena which take place in the material. That is leading to a problem formulation for a freeze–thaw situation and the formation of numerical models, which are called later “descriptive models”. These models are usually compared retrospectively with the experimental data in order to assess their validity.
- The implementation of data experiments in models to predict the macroscopic behaviour of concrete subjected to severe external conditions. That is leading to the construction of models that are called later “predictive models”.

2. Descriptive models

2.1. *Definition of the materials scales*

First of all, here the definition of the scales chosen to simulate concrete. Macroscopic scale is order of [cm] at which concrete’s components can nit be distinguished and concrete is considered like a continuum material. Microscopic scale is order of [m] at which cement paste’s components can be distinguished and capillary pores are observed. Mesoscopic scale is, by using the greek definition of ‘meso’, between the macroscopic scale and the microscopic scale. It is order of [mm] at which aggregates and sand grains cand be distinguished.

Frost damage analysis is associated to multiple scales as physical phenomena at the microscopic or mesoscopic scale affect the macroscopic properties of the material. The study scale provides a first distinction between freeze–thaw models. At the macroscopic scale, some models suggested to consider implicitly concrete's components [23,24] and calculated local strains and stresses fields which were then homogenized to define the global mechanical behaviour. Most numerical models work at mesoscopic scale by considering a volume whose size allows calculating global variables while accurately characterizing phenomena occurring within concrete [25–28]. For example, Wardeh and Perri [25] and Zuber and Marchand [26] calculated an average value of the macroscopic pressure variation $\dot{p}$ in the volume to define the pore pressure:

$$\dot{p} = \dot{p}_l + \frac{1}{n} \int_{Rp(t)}^{\infty} \dot{\chi}(r,t) \frac{d\phi}{dr} \, \mathrm{d}r \tag{1}$$

where $\dot{p}_l$ represents the variation of the liquid pressure, n the total porosity of the porous material, $R_{peq}(t)[nm]$ the curvature of the liquid/solide interface, $\frac{d\phi}{dr}dr$ the cumulative volume of pores with a radius greater than r and $\dot{\chi}(r,t)$ the variation of the stress applied on the solid by the penetration of the ice crystal. $R_{peq}(t)$ can be calculated according to the following relations [29]:

$$\text{Freezing: } \Delta T < 0 \qquad Rp = 0.584 + 0.0052T - \frac{63.46}{T} \tag{2}$$

$$\text{Thawing: } \Delta T > 0 \qquad Rp = 0.757 + 0.0074T - \frac{33.45}{T} \tag{3}$$

where $T(°C)$ represents the temperature.

To take into account the influence of aggregates on the strength of the material against freeze–thaw cycles, Rahman and Grasley [30] considered a sphere made of aggregate and surrounded by the cement paste. At the microscopic scale, in order to characterize the formation and propagation of specific micro-cracks due to freeze–thaw cycles at the particles scale, Liu et al. [31] used a lattice model to connect hydrated particles of the material. This leads to the definition of a local damage criterion governing the micro-cracks formation. An another approach is based on physics concepts of fracture and studied the growth of micro-cracks between pores [32].

2.2. *Classical assumptions*

2.2.1. Assumptions associated to thermal and thermodynamic conditions

A common assumption is to consider isothermal conditions. Indeed, as explained by Rahman and Grasley [30], we can consider that the time constant for the setting of the thermal equilibrium is smaller than the fluid movement; so the temperature field is uniform. Moreover, the supercooling phenomenon is often ignored [26, 31]. Models for the water flow into the porous structure make the assumption of laminar flow, which allows the application of the Darcy's law. The most common assumptions to simplify the models are:

- The non consideration of water vapor or to consider that it is not significant in the freeze–thaw phenomenon,

- The consideration of saturated conditions; this is a very common assumption given by standards. Models used to study the behaviour of unsaturated concrete often refer to a generalization of the equations developed in the saturated case [28].

2.2.2. Assumptions according to the porous network

The internal micro-structure of concrete could be determined by image processing obtained by Scanning Electron Microscopy [32] or Tomography [31]. But these techniques do not give information on the smallest pores ensure the connection between bigger pores. So they have to be assumed virtually or determined algorithmically.

In addition, pores of size more than 2 μm are not observed in simulations and particles less than 1 μm are neglected. These assumptions for simulations also explain the differences between the porous network and data obtained by mercury porosimetry tests.

Regarding geometric aspects, models often consider pores with spherical or cylindrical shapes. Zuber and Marchand [26] recalls that the influence of this assumption on the final result is secondary. The hypothesis may also focus on the shape of micro-cracks, which are treated as cylinders [31]. This latest study is also the only one which takes into account the influence of the newly formed micro-cracks on the material evolution, integrating the new shape of the porous network at each numerical iteration. The consideration of the same size for all pores can greatly simplify the calculations [28]. However, it is possible to take into account the difference between the pores radii and they are used as a correction factor for the liquid degree saturation S_l to govern the mass transfer [30].

2.3. Coupling methods

Most of models are based on thermodynamics and mechanics laws, but they differ in how the basic laws are coupled. At the thermodynamic level, the Gibbs–Thomson relation is usually used:

$$r = \frac{2\gamma_{CL}}{(T_m - T)\Sigma_m} \tag{4}$$

where T_m represents the fusion point, r the curvature radius, γ_{CL} the surface tension and Σ_m the fusion entropy.

2.3.1. Thermo-mechanical coupling

Coussy and Monteiro [28] used the Gibbs–Thomson relation to determine the liquid volume fraction to extend the equations obtained for poro-mechanical models developed by Biot to unsaturated conditions. This model allows obtaining three coupled equations giving the stress evolution (σ) in function of the displacement (or total strain (ε)), pressure conditions (p), temperature and porosity:

$$\sigma = K\varepsilon - b(S_c p_c + S_l p_l) + 3aK\Delta T \tag{5}$$

$$s_{ij} = 2Ge_{ij} \tag{6}$$

$$\varphi = \varphi_c + \varphi_l = b\varepsilon + (S_c p_c + S_l p_l)/N + \alpha_\phi \Delta T \tag{7}$$

where K represents the stiffness of the porous material, b the Biot's coefficient, S_c, respectively S_l, the volume fraction of ice crystal, respectively of liquid water, p_c the ice crystal pressure, α the thermal volumetric dilation coefficient of the porous media, G the shear modulus, s_{ij} and e_{ij} the components of the deviatoric stress and deviatoric strain tensors, φ the variation of the total porosity defined by a porosity part filled by the ice crystal (φ_c) and a part filled by the liquid water (φ_l), α_ϕ the thermal volumetric dilation coefficient of pores and N the Biot's modulus. These relations could also be coupled to the mass and heat conservation [33].

Koniorczyk et al. [34] have considered fully saturated materials and the Everett's equation for th ice crystallization. The hydraulic flow was simulated by the Darcy's law and damage was calculated by applying the Mazars' model:

$$\sigma = (1 - d)D(\varepsilon - \varepsilon_{th}) \tag{8}$$

where ε_{th} represents the thermal strain field defined by:

$$d\varepsilon_{th} = I\frac{\beta_s}{3dT} \tag{9}$$

where I represents the identity second order tensor and β_s a thermodynamical invariant which gives the density variation of the solid matrix according to the temperature variation ($\beta_s = 1/\rho(\Delta\rho/\Delta T)$.

The model developed by Wardeh and Perri [25] is similar to that of Koniorczyk et al. [34] by linking the mass conservation, the Darcy's law for the water flow, the change state relation of water and the Biot's relationship between stress and pressure in pores.

Liu and Yu [27] has developed a model for soil involving three coupled phenomena: thermal, defined by the Fourier's law; hydraulic, defined by the Richard's law in which a term corresponding to the ice formation is added; the strain field, highlighted by the Navier–Stokes law. Li et al. [35] have used the same type of model but the porous network was built by using the mercury intrusion prosimetry (MIP). Internal damage was also calculated in this model.

2.3.2. Implementation of the Gibbs–Thomson relation in mechanical models

Ng and Dai [32] used the cohesive zone model (CZM) to study the micro-cracks. Commonly for cementitious materials, the authors used a bilinear cohesive law. In addition, the relation (4) allowed calculating pressure on pores and calculating the behaviour of cohesion areas.

Based on the connections between particles, Liu et al. [31] provided a model fo which concrete is considered as a lattice structure. This helps them to reduce the problem to a set of equations of materials strength. Calculation of stresses in bar elements involves the relation (4). A failure criterion is applied to bar elements to characterize the formation of micro cracks. Thereafter, the displacement of each node provides the new position of the particles in the simulation. The model also includes a thermal shrinkage of the solid due to temperature variations.

2.3.3. Mechanical models

Hain and Wriggers [24] have performed their simulation at a microscopic scale to consider only mechanical phenomena. A simplified constitutive equation of the material is suggested: the behaviour of the material is substantially resilient to a certain point at which micro-cracks are formed, resulting in plasticity effects. At the macroscopic level, concrete is considered to be saturated and cut in microscopic volumes in which calculations are performed. The mechanical properties are derived by statistical techniques. At the material level, the model also takes into account thermal effects.

2.3.4. Thermodynamic models

In accordance with the theory of porous media (TPM), Kruschwitz and Bluhm [23] considered concrete as a mixture as defined in chemistry. Calculations are based on the equilibrium equations between the components and the second thermodynamic's law. The equilibrium equations take into account the components movement, but the acceleration is neglected, which is equivalent to assume that the flow is slow. The reduced equations system to be solved includes mass balance, the momentum and the energy of the mixture and the saturation condition of the solution.

2.4. Boundaries conditions

Solving mathematical equations often leads, like in the work of Zeng et al. [33], to impose boundary conditions such as Dirichlet on at least three sides of the sample: for the fluid pressure and temperature. Three pressure conditions were tested to highlight the importance of the boundary conditions [25]. In this later work, it was also assumed that the ice is formed at an outer surface of the sample, and therefore at atmospheric pressure. This assumption was also retained by Rahman and Grasley [30] and the emphasis is on the continuity of the pressure field.

Concerning the temperature decrease, Kruschwitz and Bluhm [23] and Hain and Wriggers [24] suggested to apply this condition to a surface in a linear manner and the other surfaces being placed under adiabatic conditions. Conditions according to the mass conservation may also be imposed: the sample could be sealed [28], or we can assume that the formation and melting of ice are only due to material exchange within the pores [23]. Liu et al. [31] have considered a condition of free expansion of the sample. Finally, the mechanical model of Hain and Wriggers [24] plays both Neumann and Dirichlet conditions on the stresses and displacements respectively.

2.5. Numerical methods of resolution

The finite element method is the numerical resolution technique most frequently used to derive equations. For example, Ng and Dai [32] built a finite element model in which the interfaces between elements can simulate cracks discontinuities. Recall that this method could be a high time consuming calculation; these are extremely important in the work of Hain and Wriggers [24] which led to the choice of reducing the macroscopic scale to many microscopic volumes.

In an another way, the finite volume method could be used [33] and the equations and boundary conditions are discretized in time and space by using the Crank–Nikolson scheme based on the finite difference method [30]. Kruschwitz and Bluhm [23] have suggested to implement transport theorems to weak the equations in order to use the finite element method. The Newmark method is also used to perform a time discretization.

2.6. Results and correlations with numerical values

2.6.1. Predominant phenomena

The authors have chosen predominant phenomena to represent the frost action and have implemented in their model the specific physical relations associated to these phenomena. Note that Ng and Dai [32] obtained good results by taking into account only the pressure of ice crystallization. But is it due to the choice of the boundary conditions or the material properties? The authors did not used all phenomena associated to the different frost action theories. For example, models developed by Zuber and Marchand [26] and Liu et al. [31] did not take into account the hydraulic pressure. But Coussy and Monteiro [28] showed that the second term in the following relation for the deformations, including hydraulic pressure, brings greater contribution:

$$\varepsilon = \varepsilon_{th} + \varepsilon_{\Delta\rho} + \varepsilon_{\Sigma_m} \tag{10}$$

where $\varepsilon_{\Delta\rho}$ represents the deformation due to the density variation between the constituents and ε_{Σ_m} the deformation due to the solid-liquid equilibrium.

It is therefore frequently considered, like in the work of Kruschwitz and Bluhm [23], that damage of concrete results from both the hydraulic, hydrostatic and osmotic pressures generated by the ice formation.

2.6.2. Validation for some models

Table 1 summarizes criteria used to validate some models. Results were satisfactory except for the predictions of the stresses fields in the material. In the work of Liu et al. [31], the difference between the real stresses and the calculated stresses was attributed to the fact that the model has a greater pores connectivity than in reality; which causes a faster ice growth. The multiscale model proposed by Hain and Wriggers [24] led to an assessment of the stresses fields in the simulated concrete sample. It allowed identifying a greater degree of damage at the surface in contact with the outside, which is set in relation to the cold growth. In addition, the model highlighted a great stress heterogeneity.

Table 1. Examples of validation criteria for some models presented above.

Model	Validation criterion
Poroelastic model [25, 26, 28, 36]	Prediction of the effect of air bubbles
Thermo-hydro-mechanical model [34]	Damage field
	Strain field
Lattice model [31]	Change in the number of microcracks
	Stress field
Cohesive zone model [32]	Crack growth
Theory of porous medium [24]	Volume fraction (scaling)

The introduction of a linear damage model, proposed by Koniorczyk et al. [34], shiws an underestimation of elastic modulus and overestimation of strain. The work of Gong et al. [36] focused on the calculation of the hydraulic pressure and strain. Comparison with experimental measurements of strain were performed; results showed that it was necessary to fit the permeability of the material according to the freeze–thaw cycles effects to obtain good numerical results.

These items highlighted that few models have been fully confronted with experiments. The few models that have made a comparison with experimental data on the basis of the determination of the stresses field have not been entirely satisfactory. However, the interest of these models is to better understand the origin and nature of the mechanisms leading to the deterioration of concrete, unlike the models presented in the next section.

3. Predictive models

With the exception of the work of Duan et al. [45], the scale considered in predictive models is macroscopic [8, 26, 37, 38]. This is to select one or more significant parameters and to assess their relevance in the durability of concrete against freeze–thaw cycles according to experimental data. However, they are not simple linear regressions because they use various mathematics theories and computer science.

3.1. Parameters taken into account in predictive models

Fagerlund [39] has developed a service-life model to describe damage into concrete during freeze–thaw cycles. The model is based on the critical water content determined experimentally. Hanjari et al. [40] have developed an empirical model based on many experiments to define specific mechanical relations for compressive and tensile strengths. The work of Jin et al. [41] is based on the existence of a strong link between the fractal dimension of the internal structure of concrete and the characterization of the voids size distribution. So the fractal dimension is related to the durability of concrete. In the work of Karakoç et al. [42], the artificial neural networks use data relating to the composition of concrete, more specifically the w/c ratio and the percentage of aggregates. The maximal number of freeze–thaw cycles is also included in the input data. Finally, Stemberk et al. [43] used fuzzy logic to assess the durability of concrete from its compressive strength, the level of loading and the number of freeze–thaw cycles.

3.2. Principle of the methods

Fuzzy logic is based on the evaluation, according to input data, of the durability level of concrete at a certain interval of values. The combination of different results allows assessing the durability. However, artificial neural networks can be described like a multitude of elementary processors connected in a predefined pattern. In general, like in the work of Karakoç et al. [42], three layers are considered in the network: an input layer, an output layer and a third layer so-called “hidden layer”. From a data set of experimental tests, they must be able to predict the behaviour of concrete which does not belong to this set. As stated by Kim et al. [44], neural networks provide good results but have the disadvantage of forming a sort of “black box” preventing how the result was obtained. However, they may be constructed so as to determine which input parameters are the most significant.

The fractal dimension of the porous network of concrete is assessed in the work of Jin et al. [41] from images of the microstructure. It is calculated according to the definition of Minkowski–Bouligand, considering spherical boxes. A regression model is then applied between the fractal dimension and the durability of concrete.

3.3. The stochastic approach

In the probabilistic model of Duan et al. [45], the medium is discretized into microscopic elements. Each element has an associated random lifetime parameter. When the exposure time of the element to freeze–thaw cycles exceeds its life, it is considered destroyed. Damage is evaluated as the ratio between the surface of the elements removed to the total surface area of the elements, and are connected to the change of elastic modulus of the material in order to obtain a macroscopic indicator. The lifetime is assumed to follow a Weibull distribution in which parameters are calibrated using experimental data. A good correlation with other data from the experiment was observed. However, the author points out that this model is applicable only for concrete without entrained air.

In the model of Fagerlund [39] internal damage is calculated by relations according to the water saturation degree and a potential service-life parameter is assessed by the following relation:

$$t_{life,pot} = [(S_{CR} - S_b)/e]^{1/d} \tag{11}$$

where S_{CR} represents the critical saturation degree, S_b the degradation saturation reached at the breaking point, e a material coefficient and d an exponent coefficient determined by the bubble size distribution. For a cement paste, S_{CR} is given by $(P - a_{CR})/P$ with P the total volume of pores and a_{CR} the critical air content.

3.4. Some results for predictive models

The fractal dimension has emerged as an effective criterion for assessing the durability of concrete. A law has been proposed to link the strength of concrete [43]: $K_m = 10^{-7} \exp^{8.8D}$, where D represents the damage scalar value. The solution proposed by Kim et al. [44] has the advantage of being integrated by finite element codes to give an assessment of the durability of concrete subjected to freeze–thaw cycles. The neural network established by Stemberk et al. [42] has been able to generalize its predictions of concrete does not belong to the same experimental set and gave correct results. The FIB model of Fagerlund [39] allows determining the required distance between air bubbles, so the required air content for the service-life of concrete under frost attacks. In the model of Chen et al. [46], damage is calculated according to the decrease of the effective Young's modulus: $d = 1 - E/E_0$ (with E the actual Young's modulus and E_0 the initial Toung's modulus). The model is also based on a Weibull distribution like the model of Duan et al.

4. Discussion

To summarize the advantages and inconvenients of the above models, it is first necessary to itemize all phenomena observed in cementitious materials when they are submitted to freeze–thaw cycles. Table 2 shows what phenomena each descriptive model takes into account. It can observed that all models take into account the hydrostatic pressure that is the main cause of deformation of cementitious materials at low temperatures. Few of them consider the hydraulic pressure because it is more difficult to calculate its effect on the global behaviour. Indeed, this pressure occurs in finest pores. Damage is not calculated in all models, alos because it is difficult to define the damage model at a small scale.

For predictive model, because they are based on experimental data, they do not take into account all phenomena and reduce the data to measurements of strain, or porosity network evolution, or particles separated from the material due to scaling. The model of Fagerlun [39] is different because it is based on poro-mechanical relations but it is also fitted on experimental measurements.

The modelling of the behaviour of cementitious materials at low temperatures is so difficult that researchers have to reduce the number of phenomena to take into account. Indeed, we observe thermal, mechanical, chemical and hydrical effects but it is not possible to define in which order. For example, the water dilation and the ice dilation have different effects during freezing than during thawing. The thermal dilation of water is negative when the temperature is below 4 $^{\circ}C$ and we can see that when the temperature decreases (freezing) the thermal strain $\alpha\Delta T$ is positive, and when the temperature increases (thawing until 4 $^{\circ}C$) the thermal strain becomes negative. At the same time, the thermal dilation of the cement paste has an inverser thermal strain. That is why it is important to take into account the thermal dilations of each components of the material. Also, it is known that Portlandite (hydrated phase of the cement paste) changes to calcite at low temperatures. It leads to new mechanical properties of the solid matrix and new porosity. So, the chemical effects have to be taken into account too.

Table 2. Phenomena taken into account by descriptive models.

Phenomenon / Models	[36]	[25]	[30]	[34]	[31]	[32]	[26]	[28]	[27]	[24]	[23]	[33]
Thermal dilation of water	-	-	-	-	-	-	X	-	-	-	-	X
Thermal dilation of ice	-	-	-	-	-	-	X	-	-	-	-	X
Thermal dilation of matrix	-	X	X	X	-	-	-	X	-	-	-	X
Chemical effects	-	-	-	-	-	-	-	-	-	-	X	-
Hydrostatic pressure	X	X	X	X	X	X	X	X	X	X	X	X
Hydraulic pressure	X	-	-	-	-	-	X	X	-	-	X	X
Osmotic pressure	-	-	-	-	-	-	-	-	-	-	-	-
Scaling effect	-	-	-	-	-	-	-	-	-	-	-	-
Water flow	X	X	X	X	X	-	X	-	X	-	X	X
Shrinkage of solid matrix	-	-	-	-	X	-	-	-	-	-	-	-
Internal damage	-	-	X	X	X	X	-	-	-	X	-	-
Air bubbles effect	-	-	-	-	-	-	-	-	-	-	-	-

To summarize, it is important to try to take into account all phenomena.

$$\underline{\underline{\sigma}}(\underline{y}) = \underline{\underline{\underline{\underline{C}}}}(\underline{y}, \underline{\underline{\varepsilon}}(\underline{y})) : (\underline{\underline{\varepsilon}}(\underline{y}) - \underline{\underline{\alpha}}(\underline{y}, T)\Delta T) - p_c \underline{\underline{\delta}} \tag{12}$$

where $\underline{\underline{\underline{\underline{C}}}}(\underline{y}, \underline{\underline{\varepsilon}}(\underline{y}))$ is the stiffness tensor of the material phases depending on the strain of phases and $\underline{\underline{\alpha}}(\underline{y}, T)$ the thermal expansion tensor of the material phases depending on the temperature. p_c is the capillary pressure which contains the information about the hydrostatic pressure, hydraulic pressure and osmotic pressure.

The osmotic pressure can be calculated by the following relation [10]:

$$\Pi_0 = \frac{R.T}{v_w} ln \frac{x_{ng}}{x_g} \tag{13}$$

where x_{ng} represents the quantity of unfrozen water in *mole*, x_g the quantity of frozen water in *mole*, R the perfect gas constant and v_w the initial water volume.

Calculations have to be performed at the pores scale, i.e., at the microscopic scale in order to take into account all pressures and the chemical effects. Also, a multi-scales approach can be used to link the calculated fields to a macroscopic behaviour.

For example, if all phenomena given in Table 2 are taken into account, but not the chemical effects, scaling and shrinkage, we can simulate the internal frost damage into a cement paste (Figure 1) and use the results to simulate a concrete wall (Figure 2). In the cement paste, damage is localized and appears fastly. But in concrete, the presence of aggregates decrease the damage intensity. In the concrete wall, we can observe that damage is linear with a high value when a continuum material is used for concrete. But if concrete is modelled by a mesoscopic approach by considering aggregates, damage is more localized and not linear with lower values. The consideration of heterogeneities allows creating crack profile which is close to reality. This model is not perfect and improvements are necessary like models presented above. New developments are in course to take into account all phenomena and to limit the fitting of data on experimental tests.

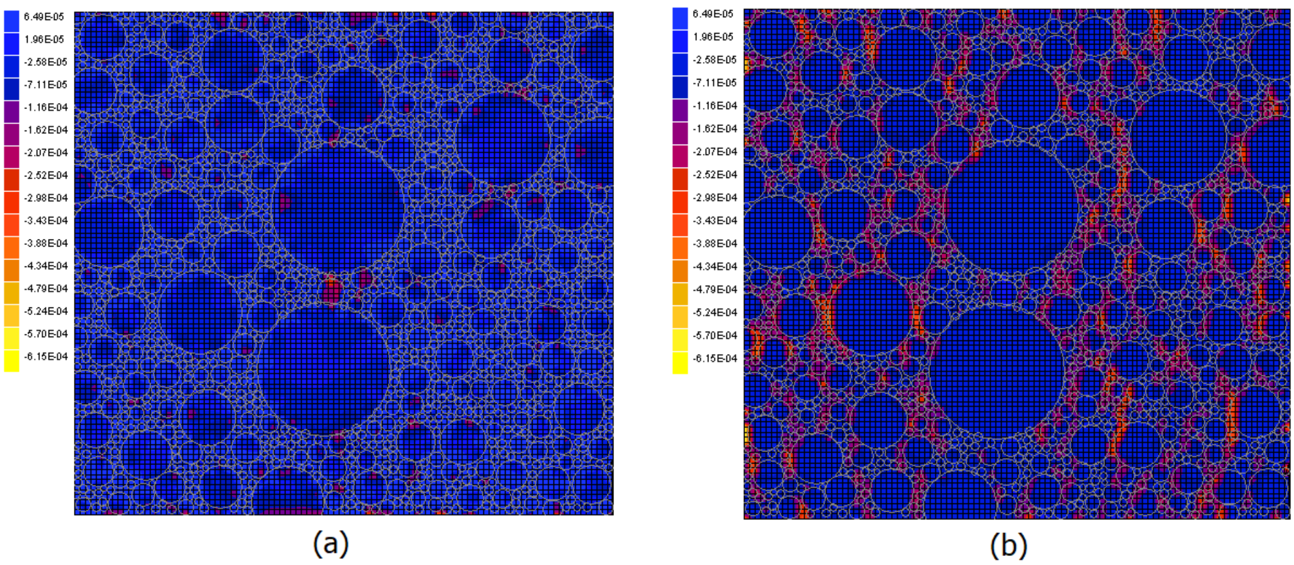

Figure 1. Strains into a cement paste with a water-to-cement ratio of $E/C = 0.6$ at $-25\ ^\circ C$ after one cycle (a) and at $5\ ^\circ C$ after 4 cycles (b).

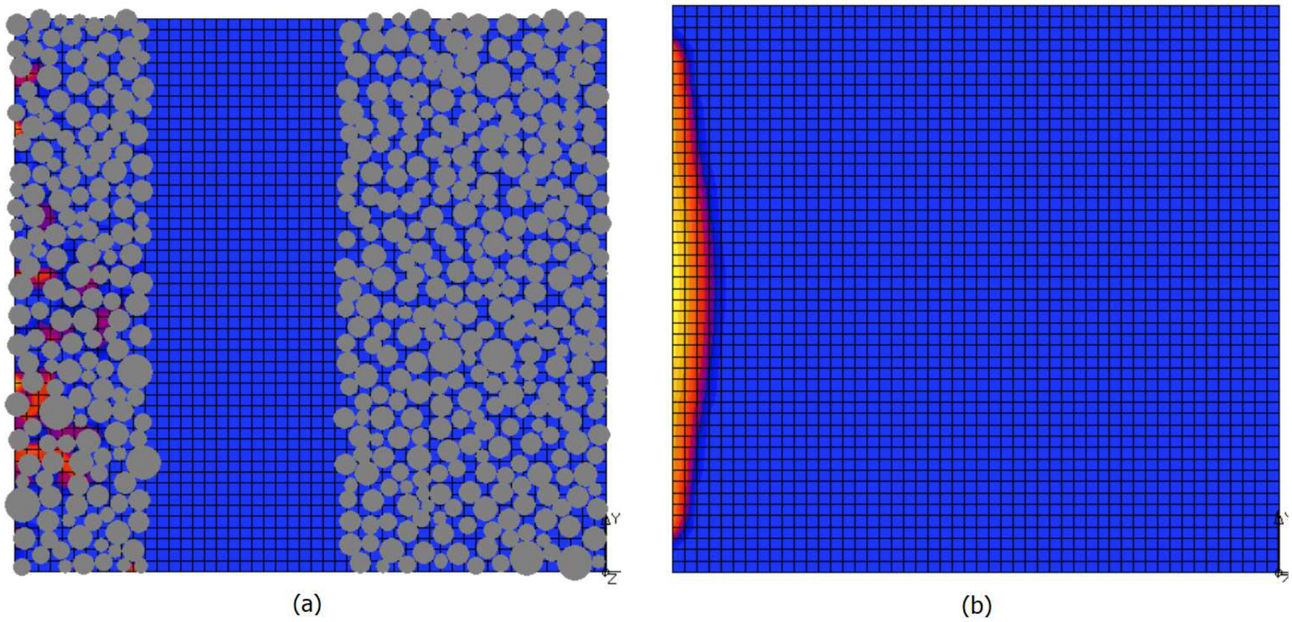

Figure 2. Damage into a concrete wall at the end of 25 freeze–thaw cycles obtained with a macroscopic continuum material (a) and with a mesoscopic material (b).

5. Conclusions

The determination of the durability of cementitious materials to freeze–thaw cycles by numerical models is fairly recent. The authors use very different methods to reach two objectives: understanding the mechanisms of the frost action and predict the durability of structures. This article aimed to summarize the different methods used in the models. The study in this paper distinguishes two families of models:

- Models with a small number of parameters are used to predict quite reliably the durability of concrete after exposure to freeze–thaw cycles, but are not of heuristic nature.
- Models that are based on the description of phenomena occurring during exposure to cold, whether at microscopic or at macroscopic scale. However, the equations obtained were either faced with little experience or showed deviations from reality. So, a complete model based on all frost theories to predict the behaviour of cementitious materials subjected to freeze–thaw cycles remains to be developed.

The methods used for modeling are based on the physical mechanisms of the cold, sometimes adapting it so as to be specific to cementitious materials. It is important to clarify that general part of physical theories is used by giving the most significant effects of frost. But all theories proposed in the past appear to be valid because they have been proven experimentally.

Conflict of interest

The authors declare no conflict of interest.

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