3D Phase Diagram for Pore Water in Cement-based Materials

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ABSTRACT

Frost damage is a serious durability problem for concrete structures in cold regions. The most original cause of this damage is the complex physical and mechanical behavior of the moisture. Thus, it is beneficial to make clear the moisture form and moisture distribution under a given environmental condition. Phase diagram is a useful tool in physics to show the form of water and phase equilibrium. By adding the pore radius to the traditional phase diagram, a three-dimensional phase diagram for pore water can be obtained. The shift of triple point and the phase boundaries can be quantitatively adjusted according to pore radius based on thermodynamic analysis. Therefore, a clear image of moisture in pores can be shown, which could be a convenient tool to get the overall moisture condition inside the material. Finally, the 3D phase diagram is used to determine the ice content at low temperature.

Keywords. pore water; phase diagram; pore size; cement-based materials; ice content

INTRODUCTION

In cold regions, frost action is a serious threat to the concrete structures. Once frost damage happens, deterioration process like chloride ion, carbon dioxide migration and even the frost action itself will be largely accelerated, result in shorter service life. Frost damage is thought caused by the internal forces generated during freezing and thawing cycles. Therefore, the moisture condition in cement-based materials is a key factor for frost action, which includes both the moisture transportation and the phase equilibrium. The moisture transportation can be explained and calculated by the potential difference, but since for the long-time estimation, the moisture condition (amount and phase) will always approach to the equilibrium condition, then it becomes quite beneficial to know the equilibrium condition if setting the certain environmental temperature and relative humidity.

The phase equilibrium of free water (other than pore water) can be well explained by the traditional phase diagram. In which the equilibrium is controlled by two factors: temperature and pressure. The condition (T, p) in which the vapor, liquid and solid phase can stay together is called triple point. For free water, the triple point is $(T_{tp}, p_{tp}) = (273.16K, 611.73Pa)$, or $(T_{tp}, RH_{tp}) = (273.16K, 1)$. RH is relative humidity, which is defined as the

ratio of the real vapor pressure to the saturated vapor pressure (p/p_s). Under the atmosphere, once the temperature falls below 0°C, all the liquid water should turn into ice; and if the relative humidity is less than 1, all the liquid water (or ice) should evaporate (or sublimate).

But for pore water, it is common that only a part of liquid water would turn into ice below 0°C and also only a part of liquid water would evaporate when the relative humidity is less than 1. This is because the pore size can alter the phase equilibrium a lot. Therefore, for pore water, besides the temperature and pressure (or relative humidity), the pore radius could be the third controlling factor.

In this paper, the equilibrium condition will be estimated based on thermodynamic analysis and the pore structure character. Furthermore, a convenient tool called "3D Phase Diagram" will be introduced to give a clearer view of phase equilibrium inside the materials.

CHEMICAL POTENTIAL OF EACH PHASE

In thermodynamics, chemical potential is a measure of potential that a substance has to produce in order to alter a system (Atkins and Paula, 2010). For the moisture transportation of liquid and vapor phase, moisture of a local place with higher chemical potential will move to the place that has lower one. And also for different phases, the phase with higher chemical potential will transform into the phase with lower one. Chemical potential is a relative concept and there is no absolute value. Therefore we choose the triple point of the phase diagram as a standard, that is, when the absolute temperature is 273K and relative humidity reaches 100%, the chemical potential of each phase is all equal to zero.

Vapor-liquid equilibrium. The expression of chemical potential of vapor phase is:

$$\mu_V = RT \ln \frac{p}{p_s} \tag{1}$$

where μ_V is the chemical potential of the vapor water (J/mol); R is the gas constant, which equals to 8.314 J/mol·K. T is the absolute temperature (K). p_s is the saturated vapor pressure under the given temperature (Pa). p/p_s is the relative humidity (RH), which can be measured in experiment. Using Kelvin equation, the relationship between relative humidity and the negative pore water pressure should be:

$$P = P_0 + \frac{RT}{v_L} \ln(RH) \tag{2}$$

where v_L is the molar volume of the liquid phase (m³/mol), P and P_0 are the absolute pressure of the liquid water and the atmospheric pressure (Pa), so $P - P_0$ is the negative water pressure (Pa). Since Kelvin equation represents the liquid-vapor equilibrium, the chemical potential of vapor and liquid phases should always be the same if Kelvin equation is satisfied. So,

$$\mu_L = \mu_V = RT \ln \frac{p}{p_s} = (P - P_0)v_L \tag{3}$$

Since the negative water pressure is caused by the surface tension of the liquid-vapor interface, there is:

$$P - P_0 = -\frac{2\gamma_{LV}\cos\theta_{LV}}{r - \delta} \tag{4}$$

where $\gamma_{LV} = 0.072\mathrm{J/m^2}$, is the specific energy of the liquid/gas interface, δ is the thickness of the adsorbed film of water on the pore wall, which is approximately equal to 0.9 nm (Scherer, 2005). θ_{LV} is the contact angle of the liquid-vapor interface. So the chemical potential of the liquid phase should be:

$$\mu_L = -\frac{2\gamma_{LV}\cos\theta_{LV}}{r - \delta} \cdot v_L \tag{5}$$

For free water, $r \to \infty$, the chemical potential of liquid phase is always equal to zero. So if the relative humidity is less than 1, means $\mu_V < 0 = \mu_L$, the moisture will automatically transfer from liquid phase to vapor phase. But for pore water with the radius of r, if $\mu_V > \mu_L$, condensation will occur; if $\mu_V < \mu_L$, evaporation will occur.

Vapor-liquid-solid equilibrium. For pore water, the freezing point of liquid water depends on the pore radius. In Scherer's paper (2005), the shift of freezing point can be derived using thermodynamics of crystallization:

$$T = T_0 - \frac{\gamma_{CL}\kappa_{CL}}{\Delta S_{fv}} \tag{6}$$

where T_0 is the freezing point of free water, which is 0$^\mathrm{o}$C. γ_{CL} is the specific energy of the crystal/liquid interface, and for ice, $\gamma_{CL} \approx 0.04\mathrm{J/m^2}$. $\Delta S_{fv} \approx 1.2\mathrm{J/(cm^3 \cdot K)}$ is the molar entropy of fusion. κ_{CL} is the curvature of the liquid-crystal interface, which can be calculated as:

$$\kappa_{CL} = \frac{2\cos\theta_{CL}}{r - \delta} \tag{7}$$

where θ_{CL} is the contact angle of liquid-crystal interface, which can be assumed to be zero. At the same time, if an ice crystal is formed, the surface tension stress of the liquid-crystal interface would also generate a negative water pressure, which equals to (Scherer, 2005):

$$P = P_0 - \gamma_{CL}\kappa_{CL} \tag{8}$$

Since the negative pressure of the liquid water contact both ice crystal and vapor should be the same, which is (Scherer, 2005):

$$\gamma_{CL}\kappa_{CL} = \gamma_{LV}\kappa_{LV} \tag{9}$$

where, κ_{LV} is the curvature of the liquid-vapor interface, which is:

$$\kappa_{LV} = \frac{2\cos\theta_{LV}}{r-\delta} \qquad (10)$$

Since the chemical potential of liquid and solid phases should also be the same if the equilibrium condition is satisfied, combine Eqs. (5), (6) and (9):

$$T - T_0 = -\frac{2\gamma_{CL}\cos\theta_{CL}}{(r-\delta)\Delta S_{fv}} = -\frac{2\gamma_{LV}\cos\theta_{LV}}{(r-\delta)\Delta S_{fv}} = \frac{\mu_L}{v_L}\cdot\frac{1}{\Delta S_{fv}} \qquad (11)$$

Therefore, the chemical potential of solid phase should be:

$$\mu_C = \mu_L = \Delta S_{fv}(T-T_0)v_L \qquad (12)$$

Thus, if in equilibrium condition, the chemical potential of vapor, liquid and solid phase could be:

$$\begin{cases} \mu_V = \mu_V(T,RH) = RT\ln(RH) \\ \mu_L = \mu_L(r) = -\dfrac{2\gamma_{LV}\cos(\theta)}{r-\delta}\cdot v_L \\ \mu_C = \mu_C(T) = \Delta S_{fv}\cdot v_L(T-T_0) \end{cases} \qquad (13)$$

A 3D PHASE DIAGRAM FOR PORE WATER

Due to the tiny scale of pore space, the phase equilibrium would be affected by the surface energy of the liquid-solid and liquid-vapor interface. Thus, the triple point and also the boundary curves for every two phases will change. If adding the pore radius as the third parameter, the traditional 2D phase diagram will change to a 3D diagram; here use $1/r$ as the vertical axis, the schematic figure is shown as in Fig. 1 (a).
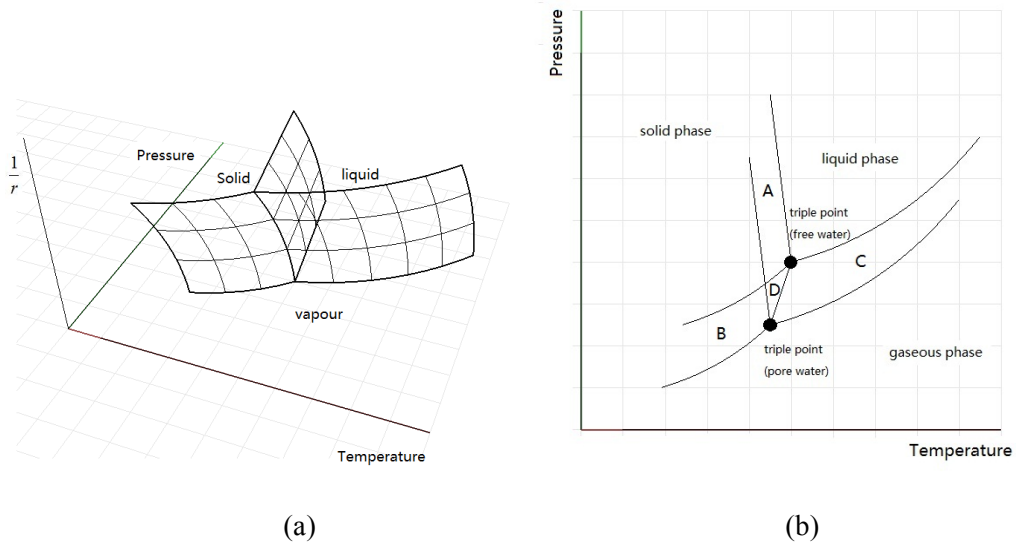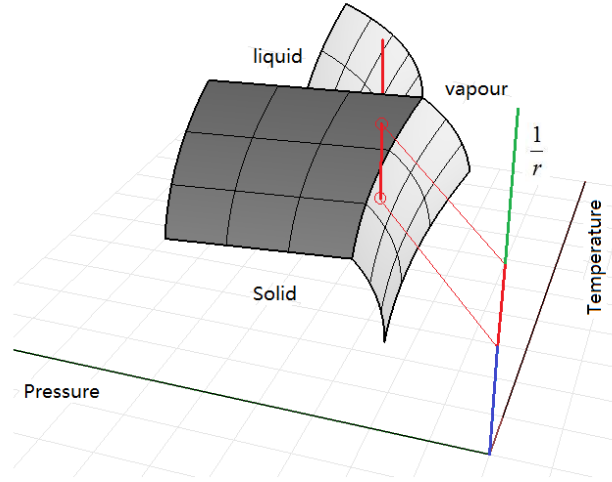

(a)   (b)

Figure 1. Concept of the 3D phase diagram (a) 3D view (b) vertial view

Since the traditional phase diagram is for free water, that is, the pore size is infinite large ($r \to \infty$). Then as the pore size decreases, the triple point will move to lower temperature and lower water vapor pressure (Fig. 1 (b)). Thus, the critical line of every two phases will change to critical surfaces.

**Figure 2. Phase of moisture in different size of pores**

So even in the same environmental condition (P,T), different pores will have different water phases. For example, in Fig. 1 (b), if (P,T) is in A zone, ice will form in bigger pores while the water in small pores is still liquid; in B zone, bigger pores contains gas and smaller ones contains ice; in C zone, bigger pores contains gas and smaller ones contains liquid water. But if (P,T) is in D zone, since the vertical line will intersect with two critical surfaces, there will be three phases in different pores (see Fig. 2). The blue, red and green parts represent the range of pore radius, which will stay in gas, ice, and liquid water respectively.

Shift of triple point. For a given size of pore, the shift of the freezing temperature can be determined by Eq. (6). The equilibrium vapor pressure regarding pore radius can be derived by combining Eq. (2) and Eq. (4):

$$p = \exp(-\frac{2\gamma_{LV}\cos\theta_{LV}}{r_p - \delta} \cdot \frac{v_L}{RT}) \cdot p_s(T) \tag{14}$$

where $p_s(T)$ is the function of saturated vapor pressure under different temperature. If the (p,T) condition in a pore with radius of r satisfy that three phase can stay together, means the temperature $T = T_0 - \dfrac{\gamma_{CL}\kappa_{CL}}{\Delta S_{fv}}$, then the equilibrium vapor pressure should be:

$$p(r) = \exp\left(-\frac{2\gamma_{LV}\cos\theta_{LV}}{r-\delta} \cdot \frac{v_L}{R\cdot\left(T_0 - \frac{2\gamma_{CL}}{(r-\delta)\Delta S_{fv}}\right)}\right)\cdot p_s\left(T_0 - \frac{2\gamma_{CL}}{(r-\delta)\Delta S_{fv}}\right) \tag{15}$$

(a)   (b)
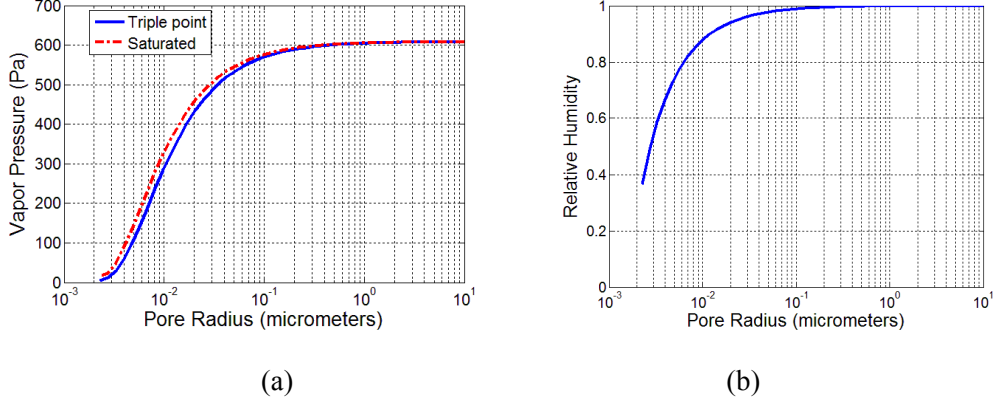
Figure 3. Vapor pressure corresponding to pore radius (a) bsolute vapor pressure of triple point and the ambient saturated vapor pressure under the corresponding temperature (b) equilibrium relative humidity (the ratio of two curves in Fig. 3 (a))

From Fig. 3, it can be seen that the absolute change of vapor pressure due to pore size is not significant, but the ratio (relative humidity) is more significant. Besides, even the relative humidity of the ambient environment falls down to 0.6, the three phases of moisture can still co-exist in the pores smaller than 3.3nm.

Boundary of every two phases. In order to quantitatively determine the 3D phase diagram, other than the triple point change, the boundary curve between every two phases with different pore radius should also be derived. Since the boundary curve means the two phases can exit together stably, the chemical potential of two phases should also be the same.

1) Liquid-vapor boundary ($\mu_V = \mu_L$), then,

$$p = p_s(T)\cdot\exp\left(-\frac{2\gamma_{LV}\cos\theta_{LV}}{r-\delta}\cdot\frac{v_L}{RT}\right) \tag{16}$$

2) Solid-vapor boundary ($\mu_V = \mu_C$), then,

$$p = p_s(T)\cdot\exp\left(\Delta S_{fv}\cdot v_L(T-T_0)\cdot\frac{1}{RT}\right) \tag{17}$$

3) Solid-liquid boundary.
   According to Scherer's paper (1999), it is necessary to impose a compressive stress on the ice if we want to prevent it from growing when temperature decreases.

$$p - p_{tp} = \int_T^{T_{tp}} \Delta S_{fv}\,dT \approx \Delta S_{fv}(T_{tp} - T) \tag{18}$$

That is, $p = \Delta S_{fv} \cdot (T_{tp}(r) - T) + p_{tp}(r)$, where p_{tp} and T_{tp} are the values of the triple point.

Actually in the real condition, the structure is usually under atmospheric pressure, so Eq. (18) is not often used, unless the materials is under high pressure, like underground or undersea structures. The phase equilibrium in high external pressure environment needs to be studied in the next study.

Discussions. Actually the absolute vapor pressure is not convenient to use. In civil engineering, the relative humidity *RH* is more often used to describe the effect of vapor pressure. Thus, for practical use, the triple point and the phase boundaries can be rewritten using *RH* in place of *p*.

Triple point:

$$\begin{cases} T_{tp}(r) = T_0 - \dfrac{2\gamma_{CL}}{(r-\delta)\Delta S_{fv}} \\[2em] RH_{tp}(r) = \exp\left(-\dfrac{2\gamma_{LV}\cos\theta_{LV}}{r-\delta} \cdot \dfrac{v_L}{R\cdot\left(T_0 - \dfrac{2\gamma_{CL}}{(r-\delta)\Delta S_{fv}}\right)}\right) \end{cases} \tag{19}$$

Phase boundaries:

$$\begin{cases} RH(r,T) = \exp\left(-\dfrac{2\gamma_{LV}\cos\theta_{LV}}{r-\delta} \cdot \dfrac{v_L}{RT}\right) & \text{liquid-vapor} \\[1.5em] RH(r,T) = \exp\left(\Delta S_{fv} \cdot v_L (T-T_0) \cdot \dfrac{1}{RT}\right) & \text{solid-vapor} \end{cases} \tag{20}$$

Fig. 4 shows the calculated diagram. The relative humidity is chosen for convenience. The two surfaces in the 3D figure represent the critical radii of each phase under any given environmental condition (*T*, *RH*). The two surfaces divide the whole space into three parts, representing different phase of moisture respectively. The value of the contour figure is the logarithm of the pore radius, for example, -8.6 means $\log_{10}(r) = -8.6$. The horizontal contour means the critical radii of empty pores and pores occupied by moisture (liquid or solid), and the vertical contour represents the critical radii of the liquid-solid interface. It can be seen that how much pores are empty is mainly controlled by the relative humidity of the environment, while how much moisture will turn into ice is mainly determined by the temperature. So from this figure, if just using one parameter (*RH* for total moisture content and *T* for ice content) to calculate the critical radii, the calculation would be much more simple, and the accuracy could still be acceptable. The black line in both figures is the critical radii when vapour, liquid and solid phase could stay together stably.
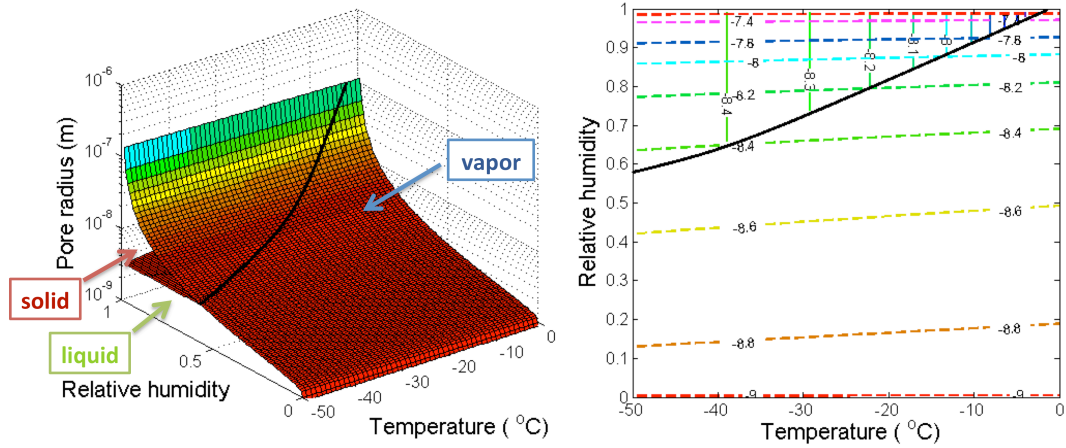
Figure 4. Calculated 3D phase diagram and critical radii

ICE FORMATION ESTIMATION

Frost damage is a serious deterioration problem for concrete materials in cold region. The internal force is caused by the freezing process of the pore water. Although there are some different mechanisms, like the hydraulic pressure proposed by Power (1945) or the crystallization pressure proposed by Scherer (2005), the ice formation is always the key point of this problem. Thus, it is beneficial to get find a convenient and clear way to get this information.

From Fig. 4, the moisture movement process (evaporation and condensation), and the ice formation process (freezing and thawing) can be approximately studied separately, which means that if the environmental relative humidity does not change much, the ice formation process is mainly controlled by the temperature. So when T reaches the freezing point T_f (calculated by Eq. (6)), the chemical potential of each phase is just the same ($\mu_V = \mu_L = \mu_C$). If $T > T_f$, then $\mu_V = \mu_L < \mu_C$, there is no ice formed. If $T < T_f$, then $\mu_V = \mu_L > \mu_C$, ice will continuously forms. Since the speed of liquid to solid phase transfer is much faster than the moisture movement within the concrete, at last, the chemical potential of liquid and solid phase should be the same, but lower than the environmental vapour phase $\mu_V > \mu_L = \mu_C$. It means that if the *RH* of the environment is high enough to satisfy $\mu_V > \mu_C$, the vapor water will continuously condensate to liquid or solid phase until the material is saturated, but this process usually take very long time so that it can be neglected during a short period.

In order to estimate the real ice content in the cement-based material, the pore size distribution is needed. But unfortunately it is not feasible to do experimental measurement every time, like using Mercury Intrusion Porometry (MIP), Nitrogen or Water Adsorption, Thermoporometry or Image Analysis. So an empirical estimation of pore size distribution is very helpful for such estimation. Here the empirical formula developed by Gong et al. (2012) is used to get the cumulated pore volume with pore radii larger than r_0:

$$V_N(r \geq r_0) = 1 - \frac{(1-k)[1+(C-1)k)] \cdot e^{-\frac{2\gamma_{LV}\cos\theta}{(r_0-\delta)RT}v_L}}{(1-k \cdot e^{-\frac{2\gamma\cos\theta}{(r_0-\delta)RT}v_l})[1+(C-1)k \cdot e^{-\frac{2\gamma_{LV}\cos\theta}{(r_0-\delta)RT}v_L})]} \tag{21}$$

Eq. (21) was derived based on the water adsorption isotherm proposed by Xi et al. (1994), which reflects the liquid-vapor equilibrium in different size of pores. V_N is the normalized cumulated pore volume (0 to 1), C and k are parameters which can be decided by Xi et al's paper (1994):

$$\begin{cases} k = \dfrac{(1-\dfrac{1}{n})C-1}{C-1} \\ n = (2.5+\dfrac{15}{t})(0.33+2.2\dfrac{w}{c})\times 1.5 \\ C = \exp(\dfrac{855}{RT}) \end{cases} \tag{22}$$

(a)   (b)
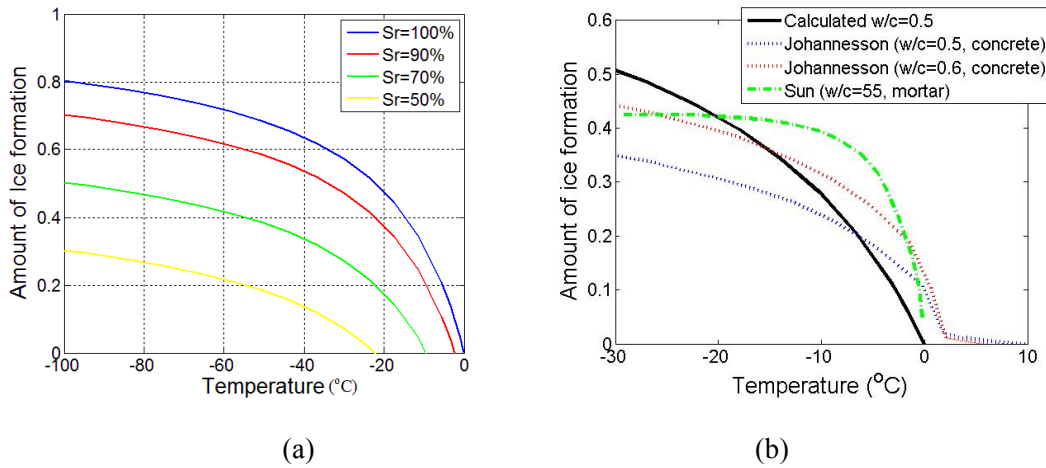
Figure 5. Estimated ice amount (a) calculated melting curve (w/c=0.5) (b) comparison with previous study

Using the pore size distribution estimated above, the ice content can be calculated for different saturation degree and temperature (Fig. 5 (a)). The calculated results show: (1) higher saturation degree results in higher ice initiation temperature and more ice content; (2) as the temperature goes down, more ice will form but the increment rate will decrease. And also some previous experiments which measuring the ice content directly by calorimeter (Jonannesson, 2010; Sun and Scherer, 2010) are compared with the calculated curve. Here the melting curves of those experiments are chosen because the mechanism of adsorption corresponds to that of melting in freeze-thaw test (Sun and Scherer, 2010). It can be seen that the calculated curve is well within the range of experimental data.

CONCLUSIONS

(1) This paper introduces the concept of the 3D phase diagram for pore water in cement-based materials, which includes the effect of pore size. This 3D diagram can give clear vision and explanation about the complex moisture equilibrium inside the materials. Not only restricted to the cement-based materials, this tool can also be applied to all kinds of porous materials.

(2) The quantitative 3D figure is drawn, the phase of moisture under any given environmental condition can be determined. The critical radii of every two phases and also the radii for three phases to stay together can be calculated. It has been found that the total moisture content, which includes both liquid and vapour phase is mainly controlled by the relative humidity. While how much of this liquid water would turn into ice is mainly determined by the temperature. So the numerical program for this problem can be improved by reducing insignificant parameters to achieve a better balance between efficiency and accuracy.

(3) The ice content can be estimated when knowing the pore size distribution. An empirical pore size distribution formula is also used to achieve this goal. The calculated results are shown, and compared with some available experimental data, but more strict experimental verification should be made in the next study.

(4) The thermodynamic model in this study is still an ideal one, in which the shape of pores has not been considered. For example, the large pore may have small entry, which makes the freezing point different. But it can be solved by introducing the pore shape information in this study, which will be done at the next step.

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