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Kinetic and thermodynamic modeling of Portland cement hydration at low temperatures

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Abstract Portland cement have to hydrate in cold climates in some particular conditions. Therefore, a better understanding of cement hydration under low temperatures would benefit the cement-based composites application. In this study, Portland cement was, therefore, kinetically and thermodynamically simulated based on a simple kinetics model and minimization of Gibbs free energy. The results of an evaluation indicate that Portland cement hydration impact factors include the water–cement ratio (w/c), temperature, and specific surface area, with the latter being an especially remarkable factor. Therefore, increasing the specific surface area to an appropriate level may be a solution to speed the delayed hydration due to low temperatures. Meanwhile, the w/c ratio is believed to be controlled under cold climates with consideration of durability. The thermodynamic calculation results suggest that low-temperature influences can be divided into three levels: irrevocable effects (<0 °C), recoverable effects (0–10 °C), and insignificant effects (10–20 °C). Portland cement was additionally measured via X-ray diffraction, thermal gravity analysis, and low-temperature nitrogen adsorption test in a laboratory and comparisons were drawn that validate the simulation result.

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Introduction

Kinetic and thermodynamic approaches have proven useful in understanding cement hydration studies (Bentz 2000; Cheung et al. 2011; Lothenbach and Winnefeld 2006), wherein the cement hydration kinetic process and hydrates could be quantitatively and thermodynamically simulated. In kinetic and thermodynamic simulations, environmental conditions could be considered in the system, such as the temperature, water–cement ratio (w/c), and air (or CO_2-free air).

The cement binder has the most significant role in Portland cement-based composites (i.e., pastes, mortars, concretes, stabilized stones, and treated soils). The cement binder properties are greatly affected by curing temperatures (Young et al. 2002) in highways, buildings, railways, tunnels, bridges, dams, and pipelines. For example, the mechanical behaviors (e.g., compressive strength, flexural strength, elastic modulus, and Poisson ratio) of hardened Portland cement concrete are enhanced by super-low temperatures, e.g., −70 to −10 °C (Lee et al. 1988). If cement-based materials are exposed to low temperature, even negative temperature (<0 °C) during the initial hydration stage, cement hydration will be greatly affected (Demirboğa et al. 2014; Nurse 1949; Saul 1951). During hydration, the hydrated products, phase converting —e.g., from ettringite (AFt) to monosulfate (AFm)—and pore solution are affected by low temperatures (Maslehuddin et al. 1997; Xu et al. 2012). In the limit, the matrix would even be damaged. Strategies should be, therefore, applied

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to avoid damages in the matrix in cold climates (ACI Committee 306 2010a, b). Chemical hydration and hardening are closely linked with the performance of Portland cement, as well the cement-based composites (Kozikowski et al. 2014; Lothenbach et al. 2008; Qiao et al. 2016; Xu et al. 2012). Thus, a better understanding of Portland cement hydration could absolutely promote the modification of cement performances under low temperatures, especially in cold climates/ regions. To this end, many studies have been conducted to elucidate the hydration of Portland cement under low temperatures (Liu et al. 2015; Nurse 1949; Polat 2016; Saul 1951).

To further clarify the low-temperature effects on the hydration process, kinetic and thermodynamic approaches were utilized to simulate the hydration of Portland cement under low temperatures. Meanwhile, the degree of hydration, as well as the hydrates, pore distributions, and mechanical behaviors, was measured in the laboratory of this study. Basically, the findings provide systematic knowledge about the hydration process of Portland cement under low temperatures, based on which some potential improving solutions will be discussed.

Experimental program

Ordinary Portland cement (OPC) was used in this study. Its oxide compositions are detailed in Table 1. It should be noted that the oxide components do not reflect the actual components in Portland cement on account of the 5–10% filler milled with clinkers. Figure 1a presents the particle distributions, while Fig. 1b shows the mineral peaks in OPC measured by X-ray diffraction (XRD). Here, PO42.5 is a type of OPC used in China containing no more than 10% mineral admixtures. The producer (Jidong Cement Plant Co., Ltd., Xi'an, China) provided the technical properties as follows: specific surface area (Blaine method) = 360 m^2/kg; density = 3.02 g/cm^3, initial setting time = 168 min; and final setting time = 282 min.

The cement pastes were mixed according to ASTM C305-14 (ASTM, 2014). They were then moved into molds (40 × 40 × 160 mm) or plastic containers. They were cured in chambers under −5, 0, 5, 8 and 20 °C (RH = 90%). It should be noted that, before mixing, raw materials (e.g., Portland cement, water), molds, and bowls had to be precooled in chambers to align with the curing temperature. For example, if the paste sample will be cured at 0 °C, the water, cement, bowls, and molds have to be precooled under 0 °C for 2 h until their surfaces reaching 0 °C. In the experimental study, the water–cement (w/c) ratio of prism samples for the strength measurement was set as 0.45, while the w/c of the paste stored in closed plastic containers was set to 0.5 for full reacting.

The pastes in the container were treated with a solvent exchange method (isopropanol) (Beaudoin et al. 1998) and then measured with XRD (Bruker, D8 Advanced, Cu-Kα), thermal gravity analysis (TGA) (TA, SDT Q600 V8.0 Build 95, Nitrogen condition), and the Brunauer-Emmett-Telle (BET) (Brunauer et al. 1938) method (Micromeritics, Gemini VII 2.00). Before the porosity test, samples were pre-heated at 105 °C for 12 h to remove the free water or other volatile components (i.e., isopropanol) in the solid.

The accurate phase dehydration temperature could be decomposed based on the derivative thermogravimetry curves. For example, portlandite (CH) could be determined between 400 and 500 °C, while $CaCO_3$ would release CO_2 from 600 to 750 °C. Therefore, the content of $Ca(OH)_2$ could be calculated based on the weight loss and decomposing temperature. However, because hydrates of $Ca(OH)_2$ are not stable and will react with CO_2 in air, thereby transforming into $CaCO_3$ (Eq. 1), the real $Ca(OH)_2$ should be calculated using Eqs. 2–4.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

$$R_{CH} = 0.74 \times R_{cc} + R_{ch} \tag{2}$$

$$R_{cc} = \frac{m_{600} - m_{750}}{m_{105}} \tag{3}$$

$$R_{ch} = \frac{m_{400} - m_{500}}{m_{105}} \tag{4}$$

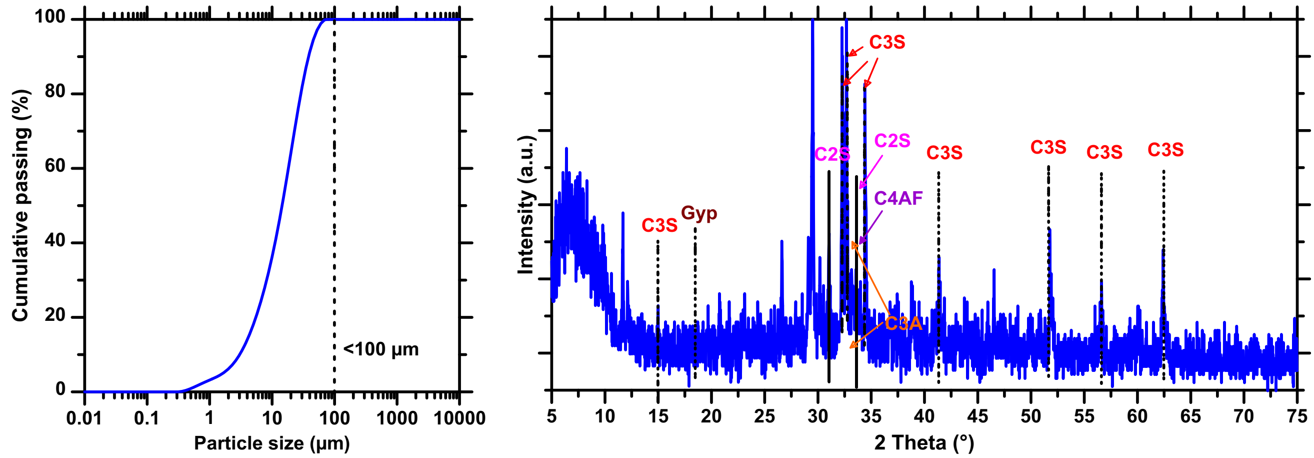
Table 1 Oxide compositions (wt.%) of Portland cement used in this study

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2
PO42.5	0.30	1.30	5.20	18.00	0.05	3.00	1.10	65.80	0.40
Oxide	MnO	Fe_2O_3	CuO	ZnO	Rb_2O	SrO	BaO	PbO	Cr_2O_3
PO42.5	0.07	4.80	0.02	0.10	0.00	0.09	0.08	0.02	0.00

Data collected by X-ray fluorescence (XRF)

In this paper, standard cement chemistry notation is used below. As per this (short-hand) notation: C=CaO, H=H_2O, A=Al_2O_3, F=Fe_2O_3, T=TiO_2, CsH_2=$CaSO_4{\cdot}2H_2O$, s=SO_3 and c=CO_2, C_3S=$3CaO{\cdot}SiO_2$ (alite), C_2S=$2CaO{\cdot}SiO_2$ (belite), C_3A = $3CaO{\cdot}Al_2O_3$ (tricalcium aluminate, Celite), C_4AF=$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (tetracalcium aluminoferrite), CH=$Ca(OH)_2$ (portlandite)

CSH Calcium–Silicate–Hydrate



(a) **(b)**

Fig. 1 Particle size and minerals of raw materials: **a** particle size, **b** mineral composition. Due to the limitation of Bogue method in which the mineral compositions (C_3S, C_2S, C_3A, C_4AF, CsH_2) of clinkers could be calculated, the Bogue phase compositions of OPC containing a part of mineral admixtures in this study is not accurate. Thus, we do not present the result of Bogue compositions

where R_{CH} is the total $Ca(OH)_2$ content ratio in solid (%), R_{cc} is the $CaCO_3$ content ratio in solid (%), R_{ch} is the experimental $Ca(OH)_2$ content in solid (%), and m_i (i = temperature, °C) is the weight of sample in TGA data. What should be noted here is that the real carbonation in total concrete life includes CH, AFm, AFt, and CSH. However, CH, AFm, AFt, and CSH are carbonated while pH = (11.6, 12.5) (10.5, 11.6), (10.0, 10.5) and pH < 10.0, respectively (Pade and Guimaraes 2007). In this study, the carbonation happened in short term, thus, the carbonated phase was supposed to be CH, wherein the others products were not considered.

To describe the hydration process of Portland cement pastes, the degree of hydration (DoH) was determined as Eq. 5 based on the Powers model (Powers and Brownyard 1946),

$$\mathrm{DoH} = \frac{m_{105} - m_{950}}{0.25 \times m_{105}} \tag{5}$$

where DoH is the degree of hydration (% by weight), m_{105} is the initial mass of sample pretreated in a muffle furnace (6 h) at 105 °C, and m_{950} is the final mass of sample heated at 950 °C.

The mechanical behaviors of hardened cement pastes were measured according to JTG E30-2005 (Test Methods of Cement and Concrete for Highway Engineering, issued by Ministry of Transport of P.R. China). It should be noted that before measurements, samples were set in a chamber with a temperature of 20°C for 1 hour.

Kinetics of Portland cement hydration under low temperatures

Hydration kinetics provides basic information on Portland cement. Many models to kinetically calculate the cement hydration have, therefore, been reported in previous studies (Camilleri 2011; Thomas et al. 2011; Tomosawa 1997; Van Breugel 1995). Basically, chemical reactions in Portland cement contain three or more reaction stages. Considering the complicated impact factors in hydration, Lin and Meyer (Lin and Meyer 2009) developed a simplified model to describe the Portland cement hydration process. In Lin's model, cement hydration is divided into two stages in which the phase boundary mechanism is assumed to be a special case of a diffusion-controlled reaction when the layers around the anhydrous cement cores are very thin. The main equations (Lin and Meyer 2009) referenced in this study are shown below.

$$\dot{\alpha} = A_\alpha \cdot \eta_\alpha \cdot \exp\left(-\frac{E_a}{\mathrm{RT}}\right) \cdot \exp\left(\frac{E_a}{293R}\right) \tag{6}$$

$$A_\alpha = k\left(\frac{A_0}{k \cdot \alpha_u} + \alpha\right)(\alpha_u - \alpha) \cdot S \tag{7}$$

$$\eta_\alpha = \exp(-n\alpha) \tag{8}$$

$$E_a = 22100 \times (m_{C3A})^{0.3} \times (m_{C4AF})^{0.25} \times (S_b)^{0.35} \tag{9}$$

while parameters in the mentioned equations were detailed in (Lin and Meyer 2009).

The information of raw material was input in the above model. Then, the degree of hydration was calculated and plotted in Fig. 2, along with the experimental data based on the Powers model. The figure shows that the simulation trend matches well with that of the experiment. Accordingly, the developed hydration degree closely related with the curing temperatures, while the higher DoH achieved higher temperatures at the same ages. However, it could be argued that the experimental plots are slightly higher than the calculated curves. This difference may be caused by the measurement methods, e.g., the dehydration using the

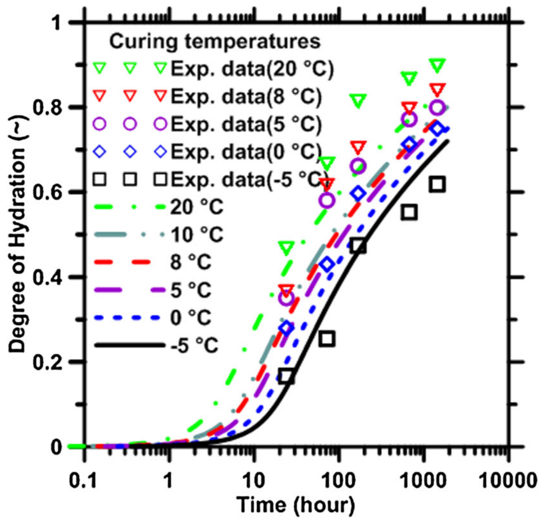


Fig. 2 DoH prediction based on kinetic modeling

muffle furnace based on the Powers model did not consider the carbonations. Thus, the measured DoH was slightly higher than the real value.

To evaluate the impact factors of Portland cement hydration under low temperatures, the hydration rate of the Portland cement was additionally calculated, as shown in Fig. 3. Here, hydration beyond 1000 h was exhibited with consideration of the specific surface area (Blaine), water–cement ratio, and environmental temperature. The result indicates the following:

1. A lower temperature slows the hydration rate of Portland cement at an early age (<30 h) on account of the low temperature reducing the chemical reactions in pastes, as declared in Eq. 6. Another reason may be that the low temperature extends the energy accumulation up to the activation energy.
2. With the same w/c and curing temperature, the specific surface area significantly impacts the Portland cement hydration, as shown in Fig. 3b. The particle size relating to a specific surface area explicitly determines the contacting area between the cement and water. Cement with a higher specific surface area or finer particles will react faster. It was believed that the particle with size >100 um could not hydrate (Young et al. 2002).
3. With a higher ratio of w/c, the contacting area between cement particles and water will be increased, resulting in a higher hydration rate of Portland cement, as shown in Fig. 3c. Overall, temperature significantly affects the hydration rate. In this case, for example, the peak of the DoH rate was more sensitive to temperature than the specific surface area and w/c ratio. Furthermore, the hydration peak moved forward with the increasing curing temperature.

Additionally, the following phenomena should be noted.

1. The specific surface area has a significant effect on the hydration rate. Compared with w/c, the specific surface area in Fig. 3b apparently shows a greater effect on the hydration rate. It should be noted that Fig. 3a presents the hydration rate under the given condition as a specific surface (Blaine) = 360 m^2/kg; w/c = 0.5. Figure 3b was obtained at 5 °C; w/c = 0.5. Additionally, specific surface (Blaine) considered for Fig. 3c was 360 m^2/kg at 5 °C. Considering the simulation conditions, however, the results do not mean that the specific surface area has the greatest effect on the hydration rate in all factors. It is a limited conclusion in this study.
2. Less of an effect on hydration rate is shown by w/c than by the specific surface area and temperature. Generally, the w/c ratio is very important for the cement-based material system. It affects the cement hydration, mechanical behaviors, sustainability, moisture transport, and so on. Thus, the effect of w/c on

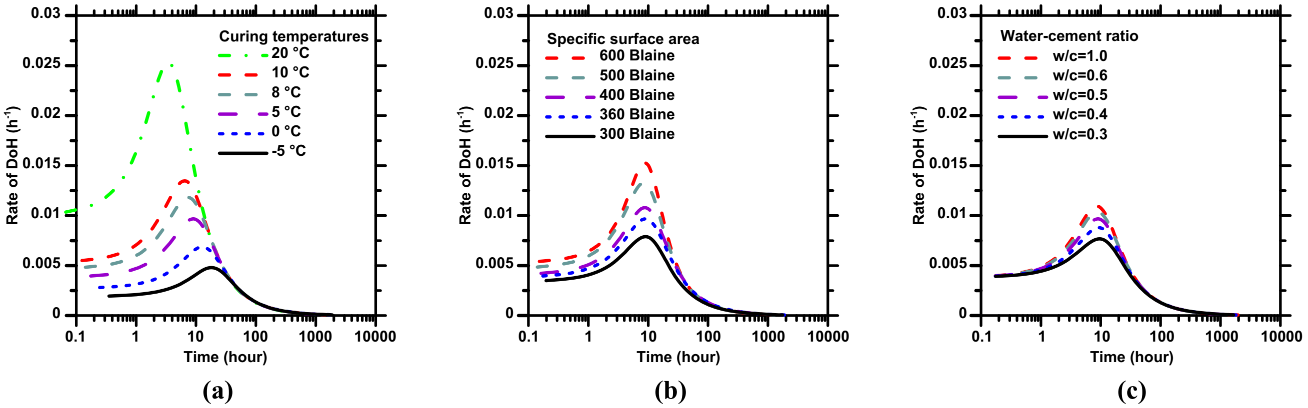


Fig. 3 Impact factors of the Portland cement hydration: **a** curing temperature effects whose w/c = 0.5, Blaine = 360 m^2/kg, **b** specific surface area effects whose w/c = 0.5, temp. = 5 °C, **c** w/c effects whose temp. = 5 °C, Blaine = 360 m^2/kg

hydration under low temperatures, even negative temperatures, is supposed. Compared with the two other factors (specific surface area and temperature), w/c shows less effect on the hydration rate in Fig. 3c. Nevertheless, w/c still relates to the mechanical behaviors and pore characteristics, which are presented below. Thus, it must balance the hydration rate and achieved strength in relation to the w/c ratio at low temperatures. Furthermore, a high w/c ratio introduces more free water in solids. Thus, damages caused by freezing would be more serious. As a result, the w/c of Portland cement concreted under low temperatures should be seriously considered, although a high w/c ratio should be avoided.

Thermodynamic calculation of Portland cement hydration under low temperatures

The thermodynamic calculation was conducted via Gibbs Energy Minimization Software (GEMS-PSI) using Gibbs free-energy minimization criteria to compute the equilibrium phase assemblages and ionic speciation of the chemical systems (Azad et al. 2016; Balonis et al. 2010; Kulik et al. 2013; Lothenbach and Winnefeld 2006). The databases of GEMS-PSI and CEMDATA7.1 were used in this study. Considering the hydration kinetics of cement, the hydration model of Parrot and Killoh (1984) was utilized (as the following equations), in which the hydration rate, R, of the individual clinkers (e.g., C_3S, C_2S, C_3A, and C_4AF) is described. It must be declared that the DoH regress equation reflected only the total hydration trend, which will be adopted in the simulations below (in Fig. 6).

In the hydration model (Parrot and Killoh 1984), the lowest value of R at curing time t is considered as the controlling step for the nucleation and growth rate

$$R_t = \frac{K_1}{N_1}(1-\alpha_t)[-\ln(1-\alpha_t)^{(1-N_1)}] \tag{10}$$

or the diffusion rate

$$R_t = \frac{K_2 \times (1-\alpha_t)^{2/3}}{1-(1-\alpha_t)^{1/3}} \tag{11}$$

or

$$R_t = K_3 \times (1-\alpha_t)^{N_3} \tag{12}$$

Based on the prediction of these equations, the degree of hydration (α_t) at time t (day) could then be calculated as $\alpha_t = \alpha_{t-1} + \Delta t \times R_{t-1}$. The parameters of K and N in the above equations were detailed in the article of Parrot and Killoh (1984), while the w/c and specific surface area were additionally considered.

Under low temperatures, the calculated degree of hydration was modified by an adjustment factor (Parrot and Killoh 1984), as shown in Eq. 13. The final stage of hydration was assumed to be 10,000 days.

$$\alpha_t = A_\alpha \eta_\alpha \exp\left(-\frac{E_a}{RT}\right)\exp\left(\frac{E_a}{293R}\right) \tag{13}$$

where the parameters could be referred in (Lin and Meyer 2009).

Actually, the chemical reaction (hydration in this study) is closely related to the environmental temperature. Thus, the thermodynamic parameters of hydrated products in the Portland cement database were calculated via the Van 't Hoff equation (Lothenbach et al. 2008), as shown in Eq. 14.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{14}$$

where K_1 and K_2 are the equilibrium constant at absolute temperature T_1 and K_2, respectively. ΔH is the reaction enthalpy. R is the ideal gas constant [8.314 J/(mol K)].

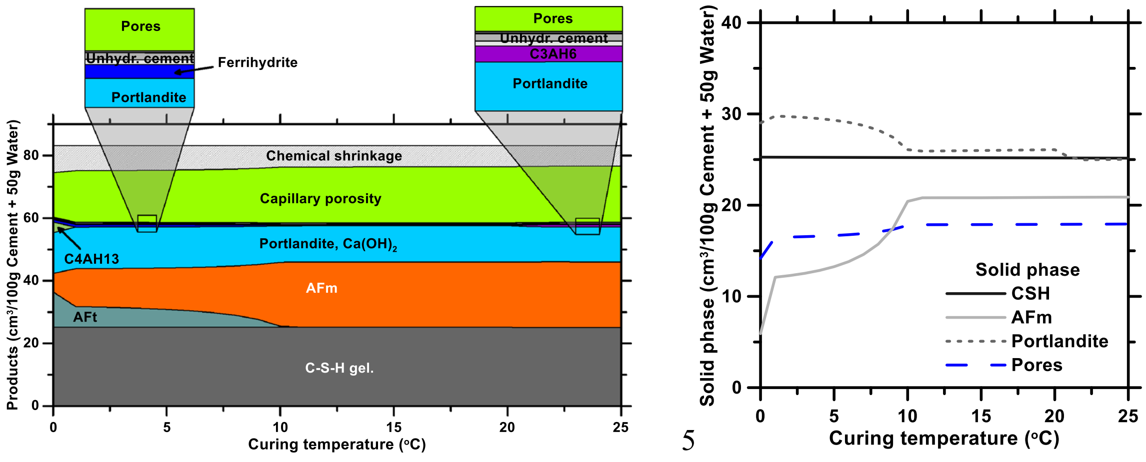
Figure 4 presents the hydrates of Portland cement under a temperature between 0 and 25 °C. As shown in the figure, with the change in curing temperature, the content of CSH (calcium–silicate–hydrate) remains stable, while the pore volume in the solid is slightly increased with the increasing curing temperature. Interestingly, the hydrates of C_4AH_{13} and AFt can be observed below 2 and 10 °C, respectively. Nevertheless, they are unstable above 10 °C and disappear between 10 and 25 °C, i.e., apparently, C_4AH_{13} and AFt converted into AFm. Figure 4b shows a slight decrease of the portlandite content around 10 °C.

It may be argued that the hydrated phases of Portland cement were reported as stable under low temperatures (0–20 °C) (Lothenbach et al. 2008). The following terms may be the main causes of these differences:

The differences between raw materials The cement used in this study was PO42.5 and produced according to the China nation criterion. However, the types used by Lothenbach et al. (2008) were SRPC (CEM I 52.5 N HTS), PLC (CEM II/A-LL 42.5R and CEM II/A-L 32.5), and OPC (CEM I 42.5 N). The composition difference, especially of SO_3 content, may engender the changes in the final products.

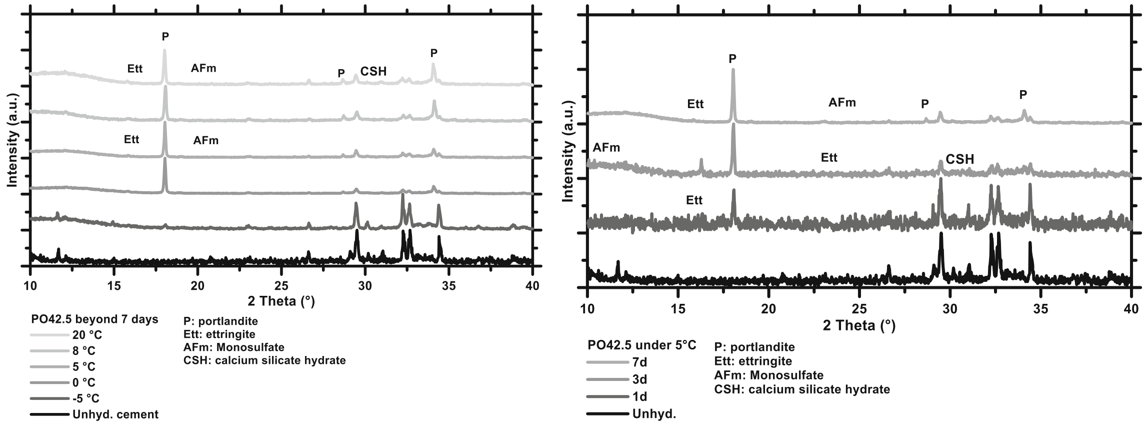
The modified parameters in hydration kinetics The hydration rate in this simulation was modified by Eq. 13. However, it differs from that of Lothenbach et al. (2008). The final degree of hydration at 10,000 days in this study should have been different considering the effects of low temperature, especially of C_3A. As a result, fewer clinkers dissolved in solutions than in the general condition (20 °C).

To verify the simulation, an experimental study was carried out in the laboratory. However, owing to the curing



(a) (b)

Fig. 4 Portland cement hydration while temperature ranges between 0 and 25 °C: **a** phase assemblages of Portland cement hydrate; **b** individual phase evolution

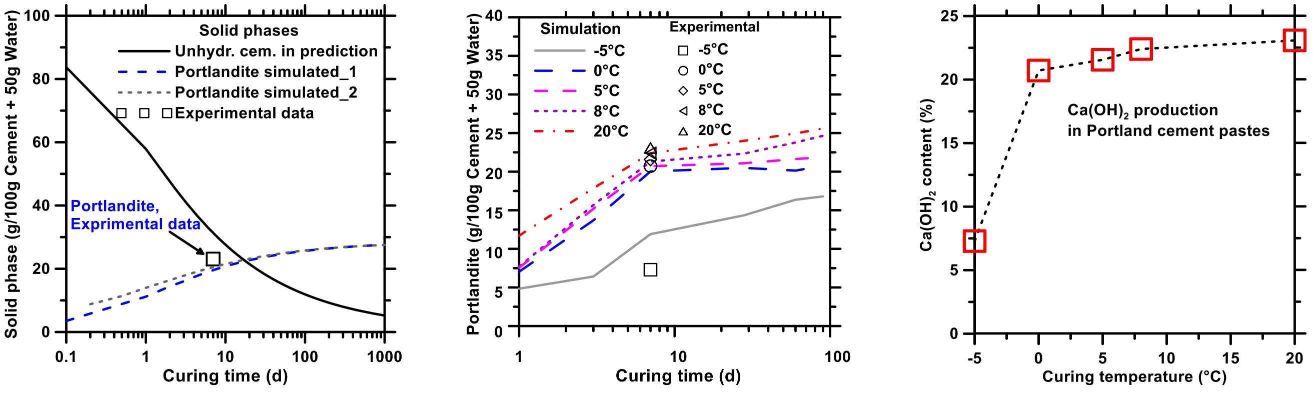


(a) (b)

Fig. 5 Effects of low temperature on the hydrates based on XRD analysis: **a** effects of curing temperature beyond 7 days; **b** phase evolution over curing time at 5 °C

age effects—i.e., the calculated age was set to 10,000 days, whereas the experimental age was limited to 30 days—the experimental data could not reveal the final hydrates of the OPC system. Nevertheless, the experimental data still provided important information and similar results. For example, the unhydrated Portland cement was reduced with the curing temperatures (Fig. 5a) and ages (Fig. 5b). Meanwhile, the peaks of portlandite ($Ca(OH)_2$) increased. This trend matches the DoH development in Fig. 2. Ettringite appeared from 1 day and then converted into AFm, which was incorporated with the ettringite behavior as simulated in Fig. 4.

Figure 6a compares the calculated data and experimental portlandite content of cement hydrates under low temperatures. The plot of portlandite is very close to the calculated curves. The dashed line marked as "simulated_1" was calculated based on the model of Parrot and Killoh (1984), while the one marked as "simulated_2" was based on the regression equations in Fig. 2. It is obvious that a small difference exists between the two models. Thus, the result in Fig. 6b was calculated based on the regression equations. The experimental plots in Fig. 6a–c were obtained based on the TGA data (The whole TGA data were presented in "Appendix"). For example, Fig. 6c shows that the portlandite content was increased over the curing temperature at 7 days. It should be noted that the $Ca(OH)_2$ calculated here includes those converted into $CaCO_3$. Based on the TGA result, the carbonation of hydrates was also affected by the environmental temperatures.

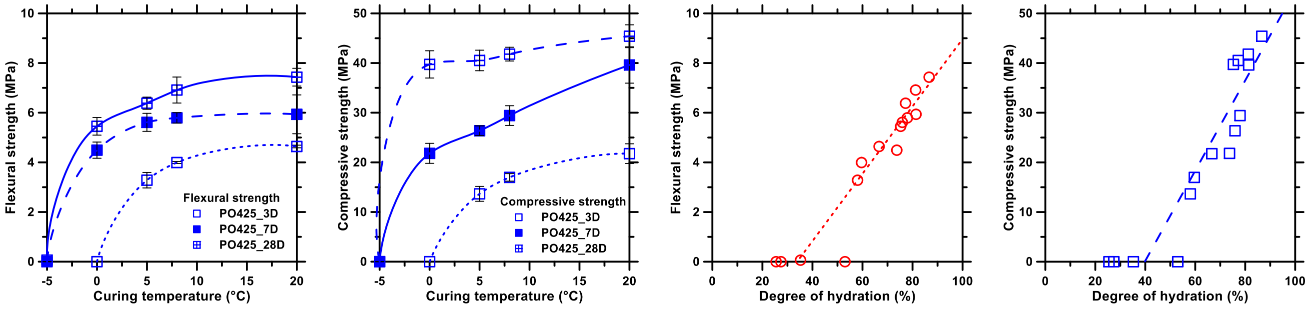


(a)

(b)

(c)

Fig. 6 Calculated hydrates and experimental data of Portland cement at low temperatures: **a** comparison of experimental and predicted data; **b** Portlandite; **c** Content of portlandite calculated based on TGA measurements. Here, the curing age of all above samples was 7 days



(a)

(b)

(c)

(d)

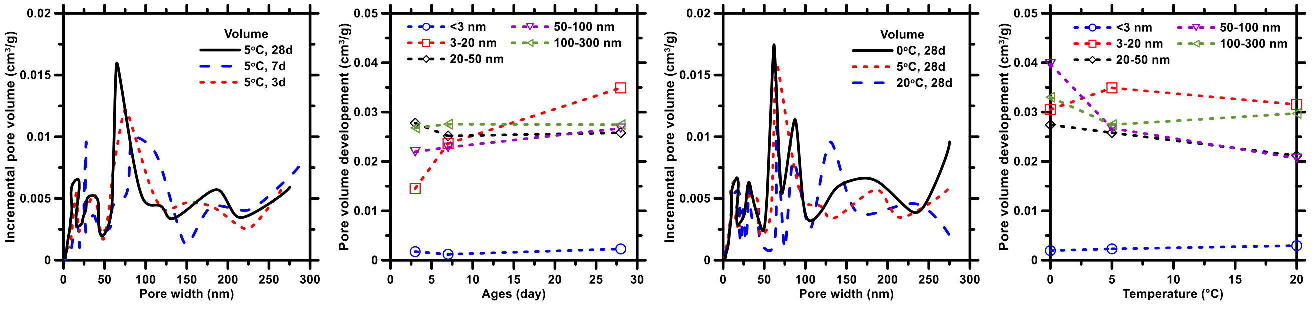
Fig. 7 Mechanical behavior development of OPC paste cured under different temperatures

Discussions

Relationships between mechanical behaviors and degree of hydration

The mechanical behaviors of cement-based building materials are very important and the primary concern of engineers in the application. Figure 7a–b demonstrates the flexural strength and compressive strength of Portland cement paste cured under −5, 0, 5, 8, and 20 °C, and then measured at 20°C. The result indicates that (1) low temperature delays the mechanical behavior development of Portland cement pastes owing to the chemical reaction and degree of hydration slowing at low temperatures. (2) The flexural strength and compressive strength of samples cured under positive temperatures (>0 °C) showed a nearly linear relationship with the curing temperatures (0, 5, 8, and 20 °C), especially for compressive strength. (3) The samples cured under −5 °C did not achieve strength regardless of early ages or late periods. The third conclusion does not match the result of DoH measured in Fig. 2, where the DoH of sample cured at −5 °C could still reach 55.3% at 28 days. The latter was similar to those of samples cured at 0 °C beyond 7 days, and 5 °C beyond 3 days. The difference shown in the mechanical behaviors was caused by the ice crystal (frozen water) formed in the interspace between hydrates. In the experimental study, the broken sample appeared as layered hydrates, while the weak linking between layers could not provide sufficient binding forces.

It was also believed that DoH has considerable linking with mechanical strength in Portland cement-based materials. Figure 7c–d shows the relationships between the degree of hydration and mechanical behaviors (including flexural strength and compressive strength). The result shows that the mechanical behavior is significantly related to the DoH, except for the sample cured under −5 °C. Moreover, the linear relationship between flexural strength and DoH seems more obvious than that between compressive strength and DoH. Thus, it can be concluded that the mechanical strength development under positive temperatures is significantly linked to the degree of hydration that slows by lower temperatures (>0 °C). However, the mechanical strength has few relationships with the degree of hydration under negative conditions (<0 °C) on account of the freezing effects.



(a) (b) (c) (d)

Fig. 8 Pore size distribution in solid Portland cement paste cured at low temperatures: **a**, **b** incremental pores distribution and typical pores development over curing time at 5 °C; **c**, **d** incremental pores distribution and typical pores development with curing temperatures at 28 days

Pore distribution in solid Portland cement pastes under low temperatures

Hydrated Portland cement is a typical porous media (Young et al. 2002). The sustainability and mechanical behaviors of these media have significant relationships with capillary pores in solids. As calculated in Figs. 4 and 5, the capillary pores were affected by curing temperatures. Owing to the limitation of measurement, the final pore distribution could not be obtained in the laboratory. Thus, the capillary porosity of hardened cement paste with an extended period (28 days) curing was measured via nitrogen adsorption at low temperature (BET), as Fig. 8 shows. The result indicates that the cumulative volume of pores decreased with the curing time addition (from 3 days to 28 days). This phenomenon was believed to have been caused by the new hydrate filling functions. For example, the main peak around 100 nm moves forward <100 nm in Fig. 8a, and the pores of <3 nm or 3–20 nm increase with the curing time.

In addition, the pore distribution of cement pastes was also affected by the curing temperatures, as shown in Fig. 8c. At a fixed curing time (28 days), the one cured at 20 °C obtained the smallest pore volume in the hydrates, whereas the one cured at 0 °C achieved the largest pore volume. At least two reasons contribute to this phenomenon:

Degree of hydration The DoH of Portland cement relates to curing conditions (e.g., temperature, moisture, pressure, etc.) and ages. As shown in Fig. 2, the DoH increases with the curing time and curing temperatures. Thus, the hydrates in paste will be promoted by the curing time and curing temperature. Meanwhile, the free water in the paste will be reduced, which consists of the capillary pores (Fig. 8).

Hydrated products Owing to the different densities of phases in Portland cement (Lothenbach and Winnefeld 2006), the volume of total solid will be changed. As the XRD data in Fig. 5 show, the hydrates of Portland cement closely relate to curing times and temperatures (Xu et al. 2012). Furthermore, the product contents in the paste also change with times and temperatures. As a result, the total volume of solids is increased.

Possible risks of durability of the Portland cement under unstable environments

The simulated and experimental results suggest that the hydrated product under 0–10 °C seemed instable on account of the pH value and *Ksp* differences affected by temperatures, which we stated as the Van ‘t Hoff equation. For example, in Fig. 4a–b, the trends and contents of hydrates show interesting changes around 10 °C, e.g., Portlandite (CH) and AFm. Additionally, another changing point of hydrates over temperatures is approximately 2 °C, where C_4AH_{13} disappears and AFm increases. Thus, risks of durability of cement-based composites might be a considerable problem under a climate with frequently changing temperature. Combined with the mechanical behaviors presented above (Fig. 7), the effects of temperature on Portland cement hydration could be divided into three levels:

Irrevocable effects (<0 °C) At this level, ice is formed in free water and the solid matrix is broken (cracked). As a result, the materials or structures will be severely damaged. The mechanical behavior of this study should be the best evidence. It should be noted that, at this level, the effects of negative temperatures could not be recovered by a temperature increase. In this stage, early strength agents (ESAs) should be considered to reduce the freezing point of solutions.

Recoverable effects (0–10 °C) At this level, because no ice and frozen breaks exist, the hydration could be continued. Thus, the mechanical behaviors continued to increase with curing time. However, owing to the low-temperature delaying of the chemical reaction and diffusions, the mechanical behaviors developed more slowly than that in the generating condition. At this level, the mechanical behavior may be lowered; however, it can still reach a good level. Furthermore, if the temperature increased up to the generating level (20 °C), the mechanical behavior should recover to the value of the generating condition. However, at this level, the regular cycles in this condition (0–10 °C) might cause fatigue-broken matrix owing to the phase conversion, in the limit, caused by phase instability. Thus, the need of air entraining agents (AEAs) exists in this range to provide sufficient spaces for potential phases transformation. As well, the AEAs benefit the durability of cement-based composites in cold climates.

Insignificant effects (10–25 °C) It is insignificant that the simulation result or experimental data indicate few effects caused by the curing temperature and temperature variation between 10 and 20 °C (25 °C in this simulation). At this level, the hydrates (Figs. 4, 5) and the mechanical behaviors (Fig. 7) will not be significantly affected. Nonetheless, a slight delay will occur in the degree of hydration. The fluctuant temperature changing in this interval will not affect the hydrate conversion or damage the matrix.

Potential improvement solutions of Portland cement under cold climates from the view of hydration

Early strength agents, e.g., $Ca(NO_3)_2$, $CaCl_2$ (Oey et al. 2014), have been widely used to promote cement hydration. However, in some conditions, special requirements may exist for material, e.g., corrosion resistance. Based on the kinetic and thermodynamic calculation above, three methods (maintained warmth, large specific surface area, and high w/c ratio) seem to work in low-temperature conditions, besides the early strength agent. Comparing the results of the specific surface area and w/c ratio, increasing the specific surface area is preferred because a high w/c ratio will decrease the strength of composites and increase the pores effect on the infrastructure durability, as discussed above.

Conclusions

In this study, Portland cement hydration under low temperatures was comprehensively examined with the approach of kinetic and thermodynamic calculation. The results were compared to experimental data. It was demonstrated that the specific surface area, w/c ratio, and environmental temperature had significant influences on the cement hydration rate in terms of the kinetic simulations. The specific surface area showed greater importance than the w/c ratio. However, this conclusion reflects only the result of this study with limited conditions. The differences between specific surface area, w/c ratio, and temperature fostered useful solutions for promoting the hydration in limited conditions. This means that increasing the specific surface area will benefit Portland cement hydration under cold regions or cold weather with low temperatures, where the w/c ratio—relating to too much free water causing harm to freezing resistance, mechanical behaviors, and durability—was not considered.

The thermodynamic simulation results agreed well with those of the experimental study, indicating that three levels of low-temperature influences exist: irrevocable effects (<0 °C), recoverable effects (0–10 °C), and insignificant effects. The mechanical behaviors under 0 °C (fresh pastes) or a frozen condition (irrevocable effects) could not recover and would be permanently reduced. On the contrary, the mechanical behaviors between 0 and 10 °C (recoverable effects) could be regained if the temperature increased to the general condition (20 °C). Nevertheless, the durability of Portland cement caused by phase changes in the limit should be discretely evaluated. The temperature of 10–20 °C (insignificant effects) will only delay the mechanical behavior development without causing permanent damage in the matrix.

It is herein suggested that, if the cement must be concreted in cold climates, strategies should be optimized according to the temperature, e.g., anti-freezing agents must be used under 0 °C. In addition, early strength agents (ESAs) could be applied, and special protections for warmth keeping or heating should be considered. Meanwhile, between 0 and 10 °C, the need exists for early strength agents (ESAs). Moreover, air entrainment agents (AEAs) should be also considered to adjust the pore distribution. Finally, for the condition between 10 and 20 °C, no further treatments exist except keeping stable curing conditions (i.e., temperature and humidity) during the curing stage, if needed.

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Appendix: TGA/DSC data of hydrated cement pastes

See Fig. 9 in "Appendix".

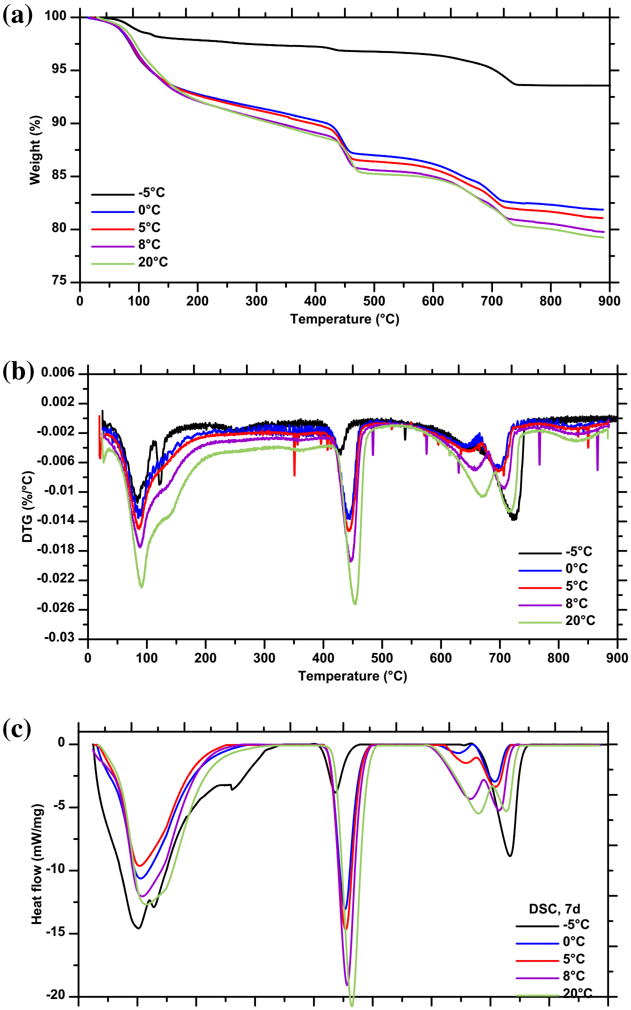

Fig. 9 TGA/DSC data of hydrated cement pastes under −5 to 20 °C: **a** TGA; **b** DTG; **c** DSC

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