

REVIEW

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Mechanical properties of concrete at low and ultra-low temperatures- a review

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Abstract

As infrastructure construction advances toward the cold and highland environment, concrete preparation technology and service performance in the cold climate is receiving much attention. The freezing of pore water inside concrete leads to significant changes in its mechanical properties at negative temperatures. Therefore, to ensure the safety of civil engineering structures in cold regions, it is necessary to fully understand the change law and enhancement mechanism of the mechanical properties of concrete and be able to predict mechanical properties at a negative temperature. Since the 1970s, scholars have studied concrete's negative temperature mechanical properties in different water-content states. This paper presents a comprehensive review of the changes in mechanical properties of concrete at low and ultra-low temperatures and further elucidates the evolution of its compressive strength, tensile strength, flexural strength, elastic modulus, and stress-strain relationship at low temperatures. It was found that the main factors affecting the mechanical properties of concrete at low temperatures were temperature and moisture content. The strength of concrete increases significantly with the decrease in temperature and the increase in moisture content. To better understand and predict the mechanical properties of concrete at low temperatures, the best model was suggested by analyzing the prediction models of different researchers and considering the dispersion of the data. Further, based on the G. Wiedemann pore model, the changes in the internal structure of concrete at low temperatures are described in detail, and the mechanism of its mechanical property enhancement is analyzed.

Keywords: Concrete, Low temperature, Ultra-low temperature, Mechanical properties

Introduction

Concrete is one of the most widely used construction materials in civil engineering [1–9], which has the advantages of abundant raw materials, easy preparation, low price, excellent mechanical properties, and can be applied to various complex environments [10–14]. With polar development, more and more infrastructure projects such as roads, railroads, bridges, and tunnels are being extended to serve cold environments.

In the 1970s, the oil crisis accelerated clean energy development and ushered in a golden development

period for the natural gas industry. The storage and transportation of natural gas also put forward higher requirements for the design and construction of large liquefied natural gas (Liquefied Natural Gas, LNG) storage tanks, i.e., the stability and reliability of the mechanical properties that concrete should have in the ultra-low temperature state of -165°C . Therefore, to carry out the structural design scientifically, rationally, and economically, and to ensure the service performance and safety of concrete structures in the severe cold environment, it is essential to clarify the evolution mechanism of the mechanical properties of concrete under low and ultra-low temperatures, to realize the prediction of its mechanical properties [15–18].

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Research significance

The mechanical properties of concrete change significantly in low and ultra-low-temperature environments compared to room temperature [19–23]. This is attributed to the fact that the pore water inside the concrete freezes at low temperatures, and the degree of freezing is affected by the room temperature, in addition to the free water content and pore structure of the concrete [24–26]. The combined effect of multiple factors also increases the difficulty of the study. Additionally, some methods for testing concrete properties do not apply to low-temperature environments. It creates more challenges for research in this field. However, studying the mechanical properties of concrete at low and ultra-low temperatures is very important to expand the application of concrete in cold regions. It is necessary to establish suitable prediction models by exploring the influencing factors and evolutionary laws of the mechanical properties of concrete at low temperatures.

To develop the use of concrete in the LNG industry, early researchers from the United States, Germany and Japan conducted a series of tests on the mechanical properties of concrete at negative temperatures. Most of the previous studies date back to 40–50 years ago, and they are scattered in the literature [16–26]. Furthermore, researchers have refocused on low-temperature concrete with the growing demand for energy and the tremendous drive for technological advancement. Different research articles have been reviewed on the performance of low-temperature concrete, which responds to the changes in concrete affected by the cold environment. However, a comprehensive review of the various mechanical properties of concrete at low temperatures is very scarce and is limited to compressive and tensile strengths [7, 9]. The water content state of concrete was not classified and summarized, which is not conducive to understanding the changes in the behaviour of concrete at low temperatures. Moreover, there is still no comprehensive explanation for the mechanism of the enhanced mechanical properties of concrete at various temperature stages at low temperatures.

Based on this, this paper summarizes the research results on the mechanical properties of concrete at low and ultra-low temperatures, mainly including the effects of negative temperature on compressive strength, tensile strength, flexural strength, modulus of elasticity, and stress-strain curve. The main factors that affect its mechanical properties are discussed, and the optimal prediction model is suggested. According to the G. Wiedemann pore model, the changes in the internal structure of concrete at low temperatures are described in detail, and the mechanism of its mechanical property enhancement is analyzed. It provides a basis for the

construction of concrete in cold areas. Finally, the direction of future research work is prospected.

Mechanical properties of concrete at low and ultra-low temperatures

Compressive strength

The compressive strength of concrete at low temperatures is higher than at room temperature. Therefore Takashi Miura et al. [24] proposed that the compressive strength of concrete at low temperature can be expressed as Eq. (1).

$$\sigma_{cl} = \sigma_{c0} + \Delta\sigma_c \quad (1)$$

Where σ_{cl} and σ_{c0} are the compressive strength of concrete at low temperature, and room temperature (20°C), respectively, and $\Delta\sigma_c$ is the increment of compressive strength (MPa).

Fig. 1 shows the relationship between the increment of compressive strength and temperature obtained by different researchers through low-temperature tests [24–44]. As can be seen, the compressive strength of concrete increases significantly with the decrease of temperature in the temperature range of 20°C ~ -196°C. The growth patterns of compressive strength at low temperatures obtained by various researchers are different due to the differences in test environments, materials, methods, and dispersion. Currently, there are two widespread viewpoints: 1) the compressive strength of concrete increases continuously with the decrease in temperature [35–40]; and 2) a critical value for the growth of compressive strength in the process of temperature drop, i.e., the compressive strength reaches a maximum value when it drops to a specific temperature. After that, the compressive strength remains constant with further temperature decline. It is generally considered that the extreme value point occurs in the range of $-120 \pm 20^\circ\text{C}$ [14, 24, 28–30].

The blue and red lines in Fig. 1 indicate the tendency lines for the maximum and minimum values of the increment of compressive strength, respectively. The difference in the increment of compressive strength is significant even at the same temperature. This is because the compressive strength of concrete at low temperatures depends on its internal moisture content and temperature dependence [14–23]. The higher the moisture content, the more significant the increase in compressive strength.

Considering the effects of temperature and moisture content on the compressive strength of concrete at low temperatures, different prediction models have been proposed by various researchers, as shown in Table 1. Browne and Bamforth et al. [28], considered that the compressive strength of concrete did not change when the temperature range was $0^\circ\text{C} \leq T \leq 20^\circ\text{C}$. When the

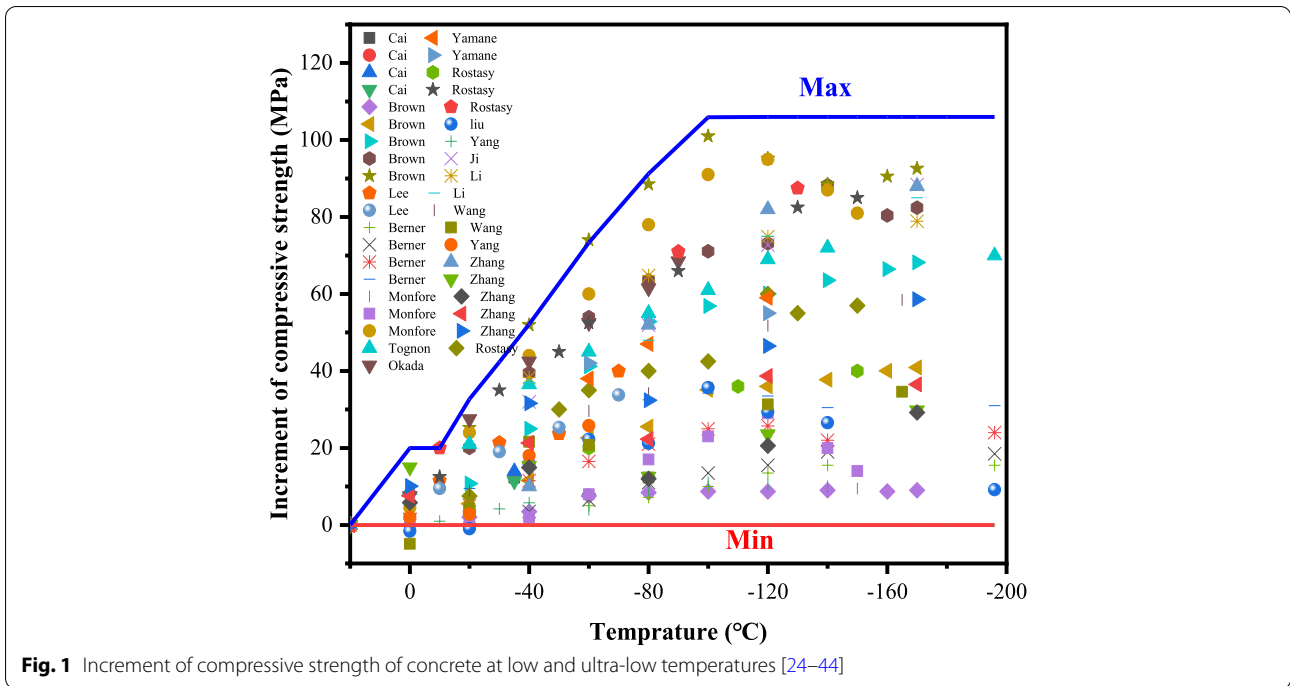


Table 1 Prediction model for the increment of compressive strength of concrete at low temperature

Researchers	Predictive Models	Rule
Browne & Bamforth [28]	$\Delta\sigma_c = \frac{-T \times W}{12}, -120^\circ\text{C} \leq T \leq 0^\circ\text{C}$ (2)	$-120^\circ\text{C} \leq T \leq 0^\circ\text{C}$, the compressive strength increases linearly with temperature and moisture content. $T \leq -120^\circ\text{C}$, compressive strength approximated as a constant value.
Takashi Miura [14]	$\Delta\sigma_c = \begin{cases} \left[12 - \frac{1}{2700}(T + 180)^2\right] \cdot W, & -120^\circ\text{C} \leq T \leq 0^\circ\text{C} \\ 10.7 \cdot W, & T < -120^\circ\text{C} \end{cases}$ (3)	$-120^\circ\text{C} \leq T \leq 0^\circ\text{C}$, the compressive strength increases with temperature decrease and moisture content increase. $T \leq -120^\circ\text{C}$, compressive strength is independent of temperature and increases linearly with the moisture content.
Rostasy [32]	$\Delta\sigma_c = 12 \cdot \left[1 - \left(\frac{T+170}{170}\right)^2\right] \cdot W, -170^\circ\text{C} \leq T \leq 0^\circ\text{C}$ (4)	$-170^\circ\text{C} \leq T \leq 0^\circ\text{C}$, the compressive strength increases continuously with a decrease in temperature and an increase in moisture content.
Shi & Liu [23]	$\Delta\sigma_c = \begin{cases} (-0.856T - 114.76) \cdot W, & -100^\circ\text{C} \leq T \leq -20^\circ\text{C} \\ (0.062T^2 + 19.86T + 2103.3) \cdot W, & -160^\circ\text{C} \leq T \leq -100^\circ\text{C} \\ (1.276T^2 + 450.66T + 39949.8) \cdot W, & -196^\circ\text{C} \leq T \leq -160^\circ\text{C} \end{cases}$ (5)	$-100^\circ\text{C} \leq T \leq -20^\circ\text{C}$, Linear growth stage. $-180^\circ\text{C} \leq T \leq -100^\circ\text{C}$, slight decline stage. $T \leq -180^\circ\text{C}$, strength recovery stage.

Note: In the table, $\Delta\sigma_c$ is the increment of compressive strength (MPa), T is the temperature ($^\circ\text{C}$), and W is the moisture content of the concrete (%)

temperature ranges from $-120^\circ\text{C} \leq T \leq 0^\circ\text{C}$, the compressive strength of concrete increases linearly with temperature and moisture content. When the temperature decreases, the compressive strength changes very little and is approximated as a constant value. Takashi Miura et al. [24] considered that the increment of concrete compressive strength at low temperatures gradually increases with the increase of moisture content. But the trends of concrete compressive strength with temperature for different moisture contents are approximately

the same. When the temperature is below -120°C , the compressive strength is independent of the temperature and increases linearly with the moisture content. Rostasy et al. [42] proposed that in the temperature range of $-170^\circ\text{C} \leq T \leq 0^\circ\text{C}$, the compressive strength of concrete at low temperatures increases with the decrease of temperature and increase of moisture content, and there is no extreme point. And unlike the models proposed by the former three researchers, Shi et al. [33] considered that the compressive strength development of

concrete at low temperatures should be in three stages: linear growth, slight decline, and strength recovery stage, respectively. The compressive strength increases linearly with the temperature decrease when the temperature is $-100^{\circ}\text{C} \leq T \leq -20^{\circ}\text{C}$; the compressive strength slightly declines when the temperature is $-180^{\circ}\text{C} \leq T \leq -100^{\circ}\text{C}$; the compressive strength recovers when the temperature is $T \leq -180^{\circ}\text{C}$.

To better verify the prediction of different models, the concrete was divided into three states according to the moisture content of the specimens in the test: wet state ($W=5\% \sim 10\%$), air-dry state ($W=2\% \sim 5\%$), and dry state ($W=0\% \sim 2\%$). Note that some of the concrete in the literature is frozen directly after standard curing at $20 \pm 2^{\circ}\text{C}$ and relative humidity of 95%, without explicitly labeling the water content of the concrete, which is classified as wet state by this paper. These four prediction models were then compared with the increments of compressive strength of concrete in different forms, as shown in Fig. 2 [24–44]. In terms of the overall trend, the three models, except for the Shi-Liu model are in general consistent with the experimental data, and all data are roughly equally distributed in the model. When considering the temperature range, only the model proposed by Takashi Miura can be applied from 0°C to -196°C . Moreover, the Takashi Miura model divides the temperature range into two segments that can concisely demonstrate the development of the compressive strength of concrete at low temperatures. Therefore, the Takashi Miura model is recommended to predict the compressive strength of concrete at low temperatures.

Notably, some of the data in Fig. 2 significantly deviate from the model for the corresponding moisture content, mainly due to two reasons. First, due to the imperfection of the test conditions, the moisture content indicated in some test data does not match the actual value. Second, the complexity of concrete, the water-cement ratio, relative humidity, pore distribution, the relationship between pore size and freezing point, and the nature of ice at low temperatures will affect the strength of concrete at low temperatures. The predictive model does not fully reflect these factors.

At the same time, with the development of concrete science and increasingly complex engineering problems, traditional concrete can no longer fully satisfy the actual needs of the construction. Fiber reinforced concrete (FRC), reactive powder concrete (RPC), engineered cementitious composites (ECC), ultra-high-performance fiber-reinforced cement-based composites (UHPC), and other new types of concrete are gradually developed. However, there are very few studies on the mechanical properties of these new types of concrete at low and ultra-low temperatures. These prediction models do

not consider these factors (concrete strength class, fiber type, fiber length, etc.). In future research, it is necessary to integrate multiple factors and improve the prediction model to serve practical engineering.

Tensile strength

Because of the unavoidable eccentricity of the specimen installation in the direct tensile test and the fact that the geometric axis of the specimen and the physical centre of gravity are not easily coincident, the splitting method is mainly used to study the tensile strength of concrete. All tensile forces in the following are splitting tensile strengths. Fig. 3 shows a summary of the relationship between the ratio of the tensile strength of concrete obtained by different researchers through low-temperature tests and the tensile strength at room temperature [22, 25, 26, 29, 33, 34, 36, 44–49]. It can be seen that almost all data are greater than 1, which indicates a significant increase in the tensile strength of concrete at low temperatures. Like compressive strength, the tensile strength is also affected by moisture content and temperature. As the temperature decreases, the tensile strength of concrete increases accordingly.

It is generally considered that the tensile strength of concrete reaches its maximum value at a specific temperature. However, the current views on this temperature differ among researchers. Bamforth et al. [26, 28, 44] suggest that the extremes occur at -70°C , while Hiedeo et al. [44] suggest that extremes occur from -30°C to -50°C . In this case, it is proposed that as the concrete temperature decreases, the pore solution gradually freezes, and a mesh structure composed of ice is formed inside. When subjected to splitting tensile loads, the ice mesh acts similarly to the fibers, and the mesh will share the load applied to the specimen. As the temperature decreases, the ice's tensile strength increases, and the concrete's splitting tensile strength also increases. However, due to the different pore structures, the ice mesh structure formed inside various concrete varies at low temperatures. The most significant difference in strength caused by the icing of the pore solution at -40°C to -80°C is the reason for the deviation in the extreme value point. As the temperature decreases further, the ice is subjected to increasing temperature stresses. When the ultimate tensile strain of ice is reached, the ice mesh structure begins to disintegrate, and the tensile strength of the specimen then decreases [37].

In general, there is a corresponding proportional relationship between the tensile strength and compressive strength of concrete, and the tensile strength is usually $1/10 \sim 1/20$ of the compressive strength. At low temperatures, the tensile strength also follows a particular

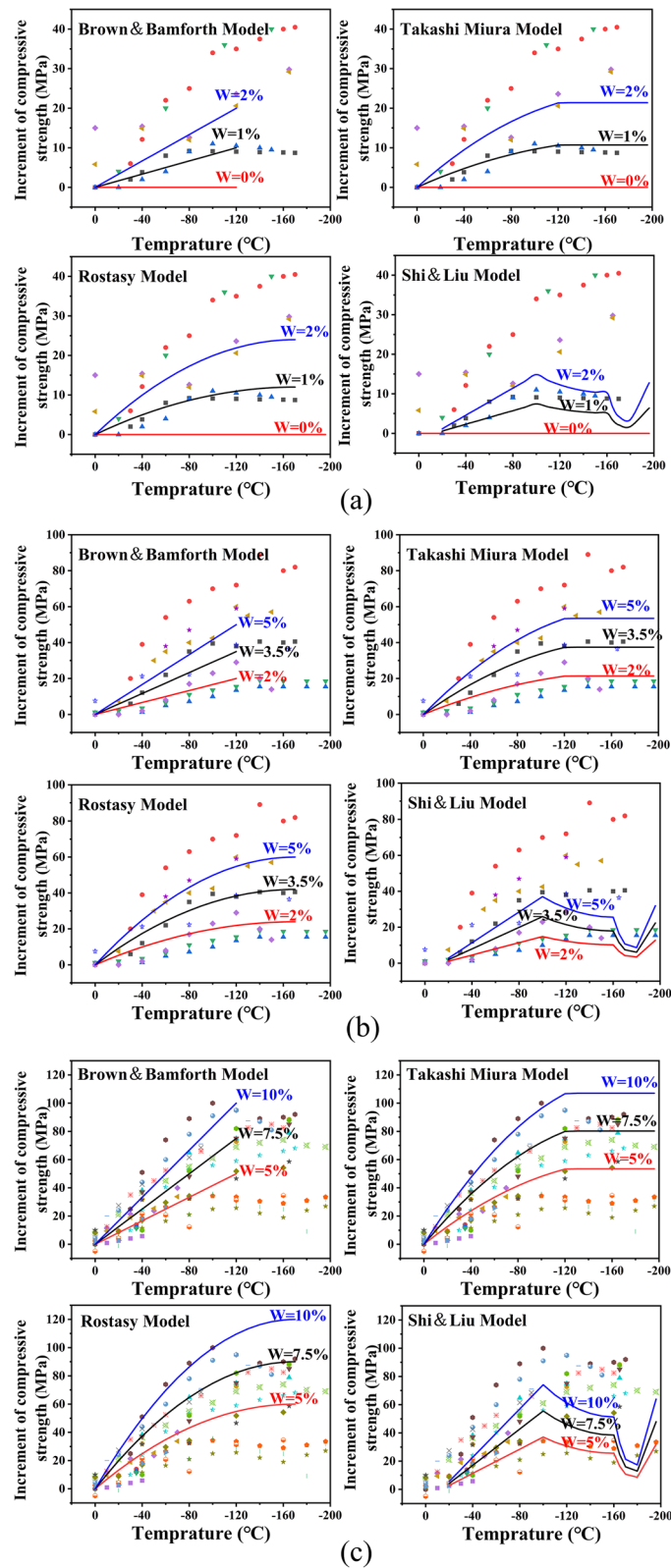


Fig. 2 Increment of compressive strength of concrete at low temperature and prediction model: (a) dry state, (b) air-dry state, (c) wet state

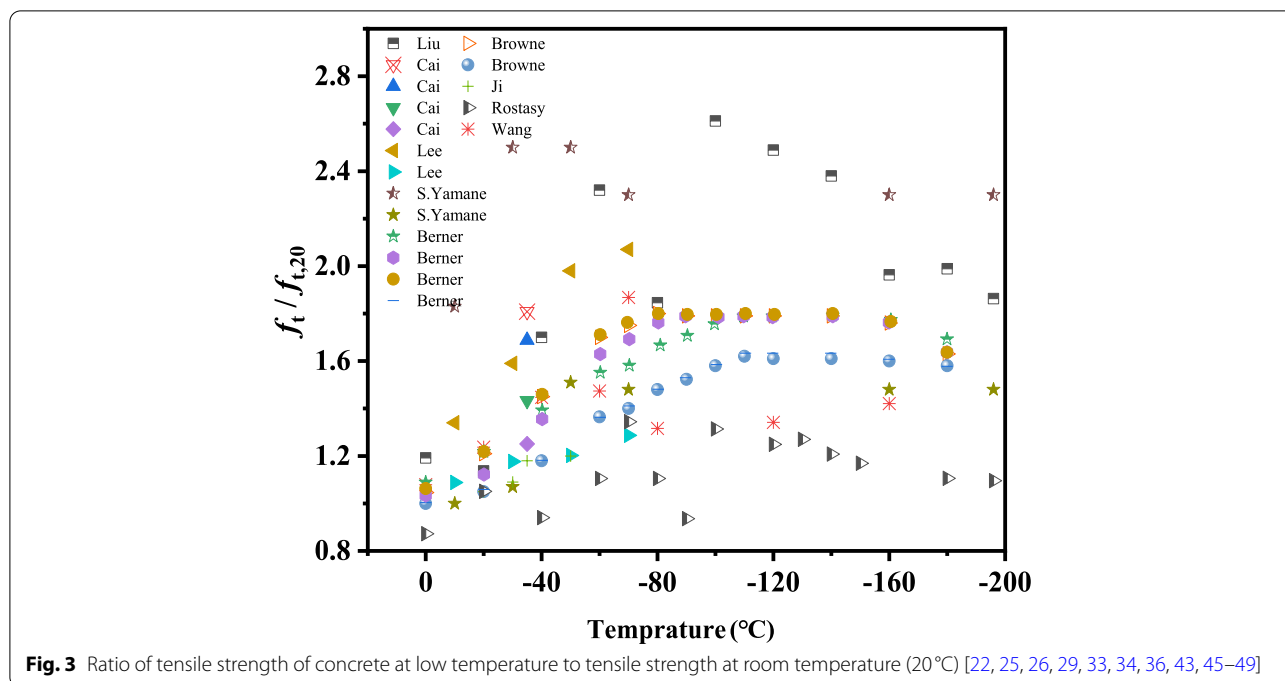


Fig. 3 Ratio of tensile strength of concrete at low temperature to tensile strength at room temperature (20°C) [22, 25, 26, 29, 33, 34, 36, 43, 45–49]

pattern. Based on this, different prediction models have been given by other researchers in comparison with the compressive strength of concrete at the corresponding temperature, as shown in Table 2. The prediction models among them are in the form of exponential functions, except for the Okada & Iguro model. Also, since the Okada & Iguro model only applies to concrete saturated with water at low temperatures, the application range is small. Considering that the water content state of concrete in the virtual environment is uncertain, the remaining prediction models are discussed and analyzed.

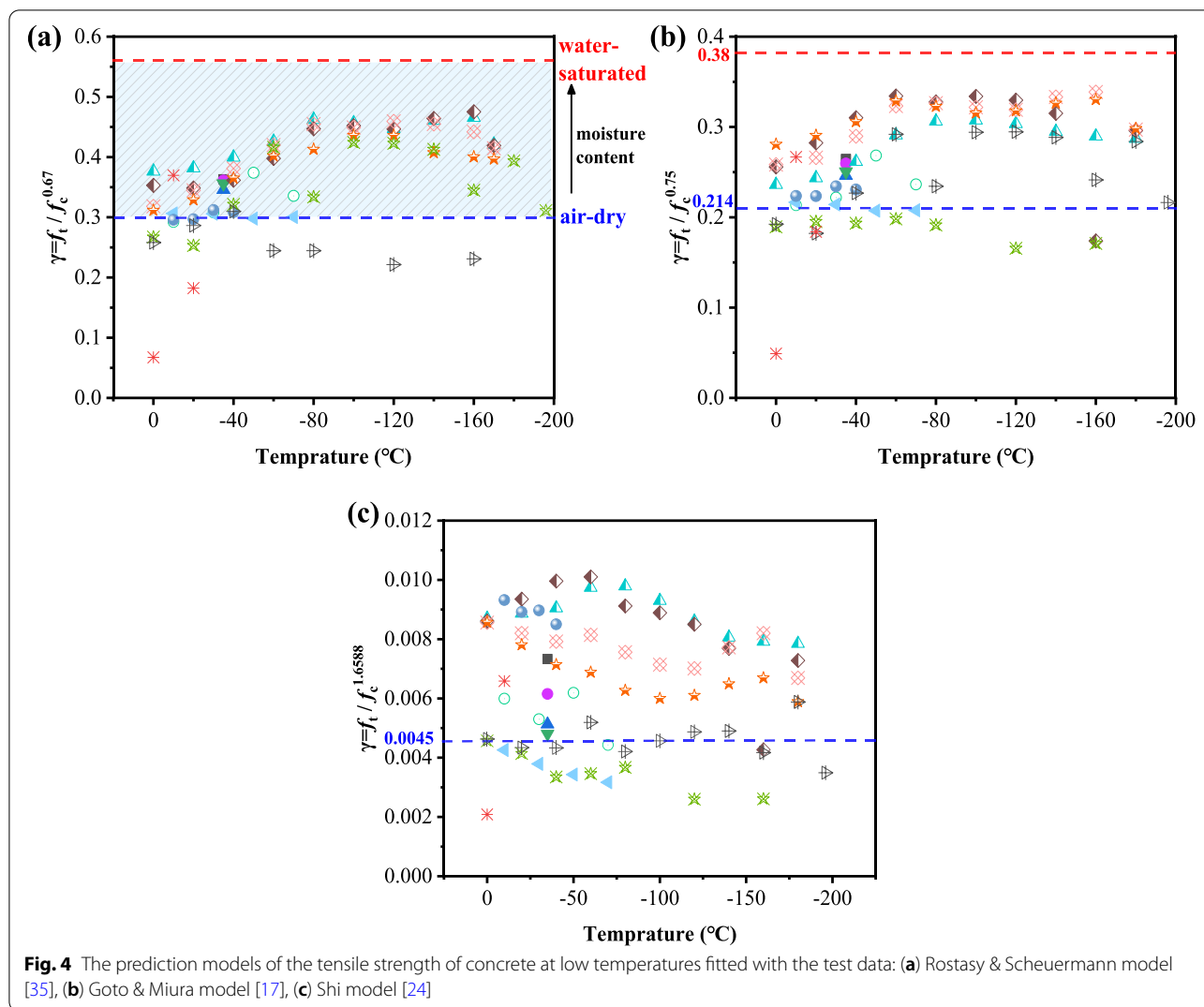
The comparison of each prediction model with the data in the literature is given in Fig. 4 [22, 25, 26, 29, 33, 34, 36, 43]. As a whole, it can be seen that the dispersion of the data is relatively small, and the tensile and compressive strengths at low temperatures are well correlated. The degree of distribution of the information is further measured quantitatively by calculating the

coefficient of variation (CV = standard deviation/mean) of the data obtained from each prediction model. The coefficients of variation in Fig. 4 (a), (b), and (c) is 0.182, 0.184, and 0.317, respectively, so it is suggested that the values of the indices in the prediction model are 0.67 to 0.75. The coefficients γ in the Rostasy & Scheuermann model are related to the water content, i.e., the concrete is taken as 0.3 in the air-dry state, 0.56 in the water-saturated state, and linearly interpolated for the rest of the conditions. This provides a better fit to the literature data and is more applicable to predicting the tensile strength of concrete with different moisture contents at low temperatures. Therefore, this paper suggests using the Rostasy & Scheuermann model to predict the tensile strength of concrete at low temperatures (Fig. 5).

In summary, these prediction models all relate the tensile strength to the compressive strength at the corresponding conditions. These relationships are

Table 2 Prediction model for tensile strength of concrete at low temperature

Researchers	Predictive Models	Notes
Okada&Iguro [22]	$f_t(T, 100\%) = 2.4 + 0.06 \times f_c(T, 100\%)$ (6)	$f_t(T, 100\%)$, $f_c(T, 100\%)$ are the tensile strength and compressive strength of water-saturated concrete at low temperature, respectively
Rostasy&Scheuermann [35]	$f_t(T, W) = \gamma \times f_c(T, W)^{0.67}$ (7)	γ is coefficient: concrete in the air-dry state to take 0.3, water-saturated state to take 0.56, the rest of the state interpolation can be.
Goto&Miura [17]	$f_t(T, W) = 0.214f_c(T, W)^{3/4}$ (8)	$f_t(T, W)$, $f_c(T, W)$ are the tensile strength and compressive strength of concrete at low temperature, respectively
Takashi Miura [24]	$f_t(T, W) = 0.38f_c(T, W)^{3/4}$ (9)	
Shi [33]	$f_t(T, W) = 0.0045f_c(T, W)^{1.6588}$ (10)	



relatively accurate for normal concrete. However, when these models are introduced into fiber-reinforced concrete, it is found that the models do not predict the tensile strength very well. In contrast, the fibers are much weaker under compressive loading, and this unbalanced effect causes the failure of these prediction models. Therefore, future studies need to introduce new parameters to modify the model to achieve accurate performance prediction.

Flexural strength

There is little research data on concrete’s flexural strength at low temperatures. It is generally believed that as the moisture content of concrete increases and the temperature decreases, its flexural strength growth rate gradually increases. However, it has also been suggested that the flexural strength does not continue to grow with a reduction of temperature and peaks at -60°C . This difference

is caused by the different porosity, pore size distribution, pore morphology, cooling rate, and strength class of the concrete, which requires further research and analysis.

Jiang et al. [50] investigated the mechanical properties of mortar at low temperatures through experiments. They found that water content was one of the most significant factors affecting the flexural strength of mortar at low temperatures. The increase of pore water on the flexural strength of mortar at ultra-low temperature was more remarkable than its growth rate on the compressive strength. He also suggested that since flexural damage is essentially tensile damage, the phenomenon that flexural strength peaks at -60°C may be related to the ice mesh structure’s dissolution [44]. Doo-Yeol Yoo et al. [45] investigated the effect of low temperatures on the flexural cracking performance of ultra-high-performance fiber-reinforced concrete. It was found that ultra-high-performance fiber-reinforced concrete had better flexural

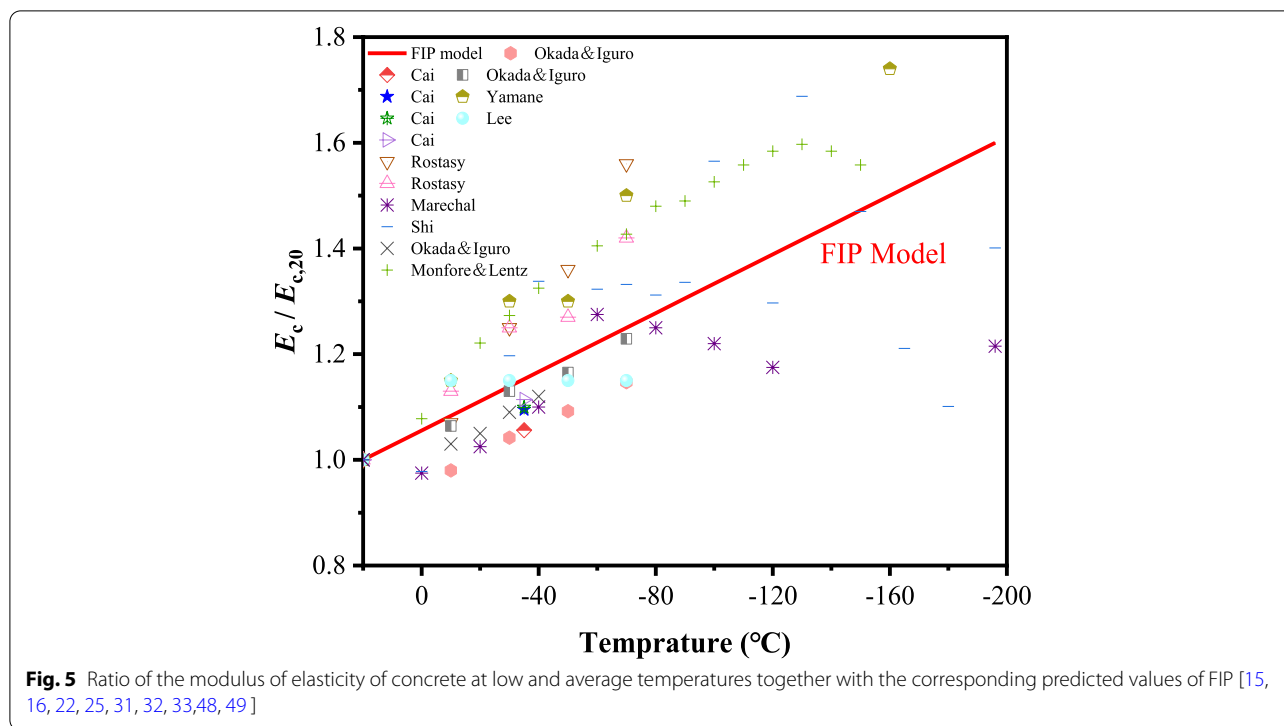


Fig. 5 Ratio of the modulus of elasticity of concrete at low and average temperatures together with the corresponding predicted values of FIP [15, 16, 22, 25, 31, 32, 33, 48, 49]

properties, including strength, flexural capacity, and toughness, both before and after exposure to low temperatures compared to normal concrete. Meanwhile, ultra-high-performance fiber-reinforced concrete has a higher resistance to microcracks during low-temperature cooling than normal concrete.

However, there is no prediction model for the flexural strength of concrete at low temperatures. Since the flexural damage of concrete is essentially tensile, this paper suggests a similar form of a tensile strength prediction model to establish a relationship with the compressive strength of concrete under the same conditions to form a prediction model of flexural strength at low temperatures. At the same time, the bridge effect of fiber may be enhanced at low temperatures, and the flexural strength of fiber concrete will change, so the multi-factor coupling effect should also be considered in the prediction model.

Stress-strain curve and modulus of elasticity

Federation Internationale de la Prcontrainte (FIP) gives the variation of modulus of elasticity with the temperature at 20°C to −196°C when the relative humidity of concrete is 86% to 100%, as shown in Eq. (11) [48]. The ratio of the modulus of elasticity of concrete at different temperatures to the modulus of elasticity at room temperature, and the predicted value of the modulus of elasticity of FIP are given in Fig. 7 [22, 25, 28, 30–32].

As shown in Fig. 7, the modulus of elasticity of concrete increases significantly with the decrease in temperature, which is linear. The predicted and tested values obtained from the FIP calculations are highly correlated. Similar to flexural strength, there is controversy about the modulus of elasticity of concrete at low temperatures. Most researchers [18, 22, 40, 43] believed that the modulus of elasticity of concrete at low temperatures increases with the decrease in temperature, and there is no extreme value. A few researchers have pointed out the existence of extreme values of the modulus of elasticity of concrete at low temperatures; Monfore and Lenz et al. [15] experimentally concluded that the power point occurs at −120°C, while Marechal et al. [31] considered that the end occurs at −70°C. This is similarly because of the discrete nature of concrete and the differences in test equipment and methods.

$$E_c(T) = E_c(T = 20^\circ\text{C}) \times \left(1 + 0.5 \times \frac{20^\circ\text{C} - T}{185^\circ\text{C}} \right) \tag{11}$$

Where T is the temperature (°C), and $E_c(T)$ is the modulus of elasticity of concrete at T temperature (GPa).

It is well known that the axial compressive stress-strain curve is one of the most basic and essential mechanical properties of concrete, which is the primary basis for studying the strength and deformation of reinforced concrete structures. It has been widely used in the fields of

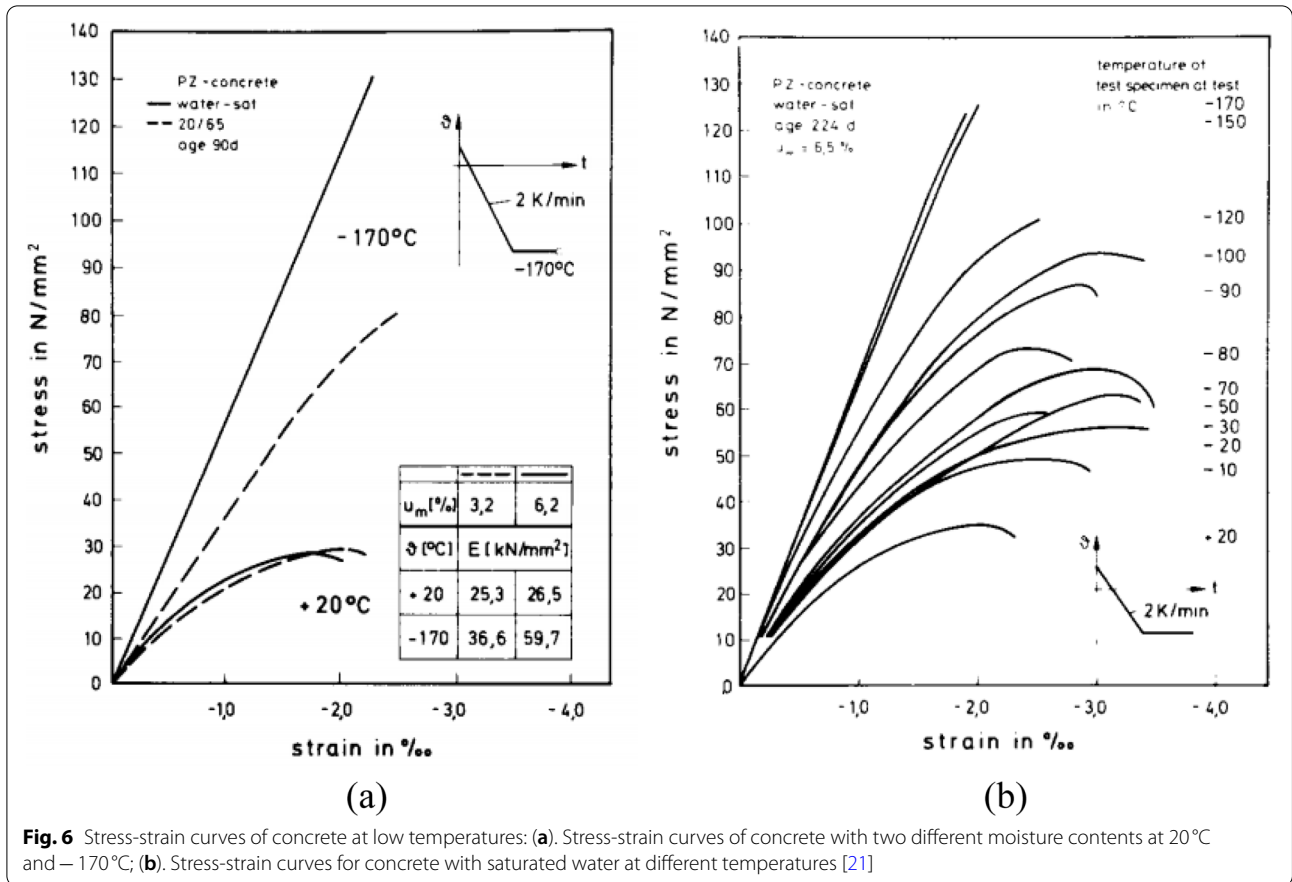


Fig. 6 Stress-strain curves of concrete at low temperatures: (a). Stress-strain curves of concrete with two different moisture contents at 20°C and -170°C; (b). Stress-strain curves for concrete with saturated water at different temperatures [21]

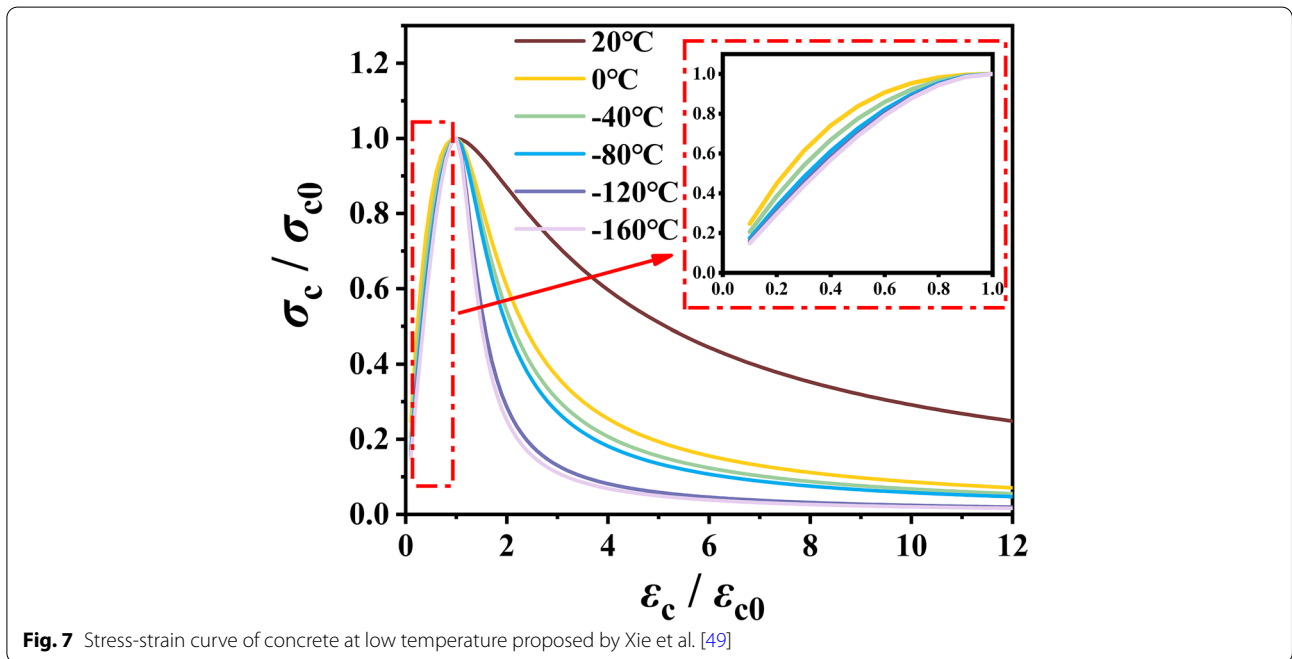


Fig. 7 Stress-strain curve of concrete at low temperature proposed by Xie et al. [49]

elastic-plastic comprehensive process analysis of members, stress distribution in the cross-section of members in the limit state, and ductility analysis of seismic and blast-resistant structures. Therefore, studying stress-strain curves of concrete at low temperatures is very important for designing and applying concrete structures in severe cold environments. The stress-strain curve of concrete at low temperatures is similar to that at room temperature. While its parameters, such as peak stress, strain, and elastic modulus, change considerably. The stress-strain curves of concrete in low temperatures at different moisture contents were studied experimentally by Rostasy et al. [21] and are shown in Fig. 6. It can be found that with the decrease in temperature, the elastic modulus of concrete increases, the peak stress increases, and the peak strain decreases. When the temperature is below -70°C , the stress-strain relationship of concrete becomes increasingly close to linear, and the trend becomes more pronounced with higher moisture content. When the temperature reaches -170°C , the water-saturated concrete stress-strain relationship is close to a straight line, the stress-strain relationship is almost positive, and the concrete is entirely elastic. The stress-strain relationship for concrete at negative temperature is also shown in Eq. (12) and (13).

$$\sigma_c(T) = f_c(T, W) \times \left[1 - \left(\frac{\varepsilon_c(T)}{\varepsilon_{fc}(T)} \right)^n \right] \quad (12)$$

$$n = \begin{cases} 2, & T = 20^{\circ}\text{C} \\ 1 + \frac{T+170^{\circ}\text{C}}{170^{\circ}\text{C}}, & -170^{\circ}\text{C} < T < 20^{\circ}\text{C} \\ 1, & T = -170^{\circ}\text{C} \end{cases} \quad (13)$$

Where $\sigma_c(T)$, $\varepsilon_c(T)$ are the stress and strain values at a point on the concrete stress-strain curve, respectively, $\varepsilon_{fc}(T)$ is the strain value corresponding to the peak stress in the concrete stress-strain curve, and n is the coefficient.

The constitutive relationship of concrete at low temperatures was studied experimentally by Xie et al. [49]. It was found that as the temperature decreased, the elastic modulus of concrete increased, the peak stress increased, the peak strain decreased, and the brittleness increased. And the corresponding parameters at low temperatures are given in Eq. (14) by combining the segmental fitted stress-strain curves proposed by Guo et al. [51], as shown in Fig. 7.

$$y = \begin{cases} Ax + (3 - 2A)x^2 + (A - 2)x^3, & 0 < x < 1 \\ x[a(x - 1)^2 + x]^{-1}, & x > 1 \end{cases} \quad (14)$$

$$\begin{cases} x = \varepsilon_c / \varepsilon_{c0} \\ y = \sigma_c / \sigma_{c0} \end{cases} \quad (15)$$

Where ε_c is the strain of concrete, ε_{c0} is the peak strain of concrete, σ_c is the stress of concrete, and σ_{c0} is the peak stress of concrete. A is the ratio of the initial elastic modulus of concrete to the cut-line modulus of concrete at the peak point, and a is the falling section parameter, which to some extent can indicate the steepness of the falling section, i.e., it is positively related to the absolute value of the stiffness of the falling branch. The importance of A and parameters at low temperatures are shown in Table 3.

Comparing the Rostasy constitutive model and the Jian Xie constitutive model, it can be found that their rising segment trends and values are approximately the same. However, due to the limitation of the test conditions, the Rostasy constitutive model only has the increasing section of the stress-strain curve without the falling area, so this paper suggests using the concrete constitutive model at low temperature proposed by Xie et al. the model is based on C60 concrete prisms and does not consider the influence of moisture content and other factors. It lacks comparison with the stress-strain curves of other strength classes of concrete, so it is necessary to verify the model's accuracy and further propose a more reasonable and perfect multi-factor constitutive relationship model.

Mechanism of strengthening mechanical properties of concrete at low and ultra-low temperatures

Phase change of pore water in concrete

Water has three phases: gas, liquid, and solid. At different temperatures and pressures, water exists in other phase states. Still, only a unique three-phase point exists, as shown in Fig. 8. When the cooling rate is too fast to reach the nucleation potential energy, water will be subcooled, i.e., remain in the liquid phase below 0°C .

The process of concrete strength development at low temperatures is the process of pore water freezing inside the concrete, the interaction between ice and pore walls, and the shrinkage of the concrete. Therefore, concrete

Table 3 Parameters of stress-strain relationship for concrete at low temperature [49]

Temperature/($^{\circ}\text{C}$)	20	0	-40	-80	-120	-160
A	2.7	2.7	2.2	1.8	1.6	1.5
a	0.3	1.3	1.7	2	5	6

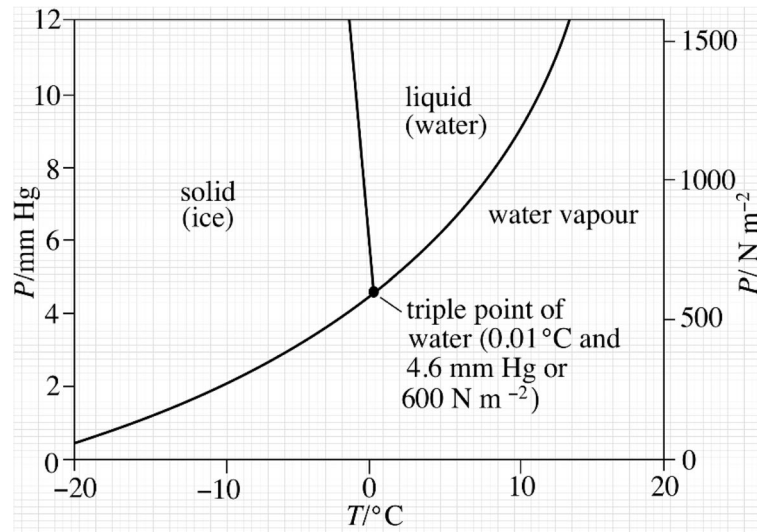


Fig. 8 Three phases of water

pore distribution, porosity, and pore size are important in developing concrete strength at low temperatures. Depending on the pore size in which they are located, the water inside the concrete is divided into the following categories [52].

- (1) Free water: When concrete is cured and storage in an environment with a relative humidity greater than 99% (wet or in water), free water fills the pores with a radius greater than 100 nm and needs to be cooled only slightly, with a freezing point of about 0°C.
- (2) Capillary water: When concrete is stored in an environment with relative humidity between 90% and 99%, capillary water fills the pores with a radius greater than 10 nm and less than 100 nm, and the freezing point is reduced to approximately -10 to -30°C.
- (3) Gel water: Gel water consists of a film of water on the solid surface and water in pores with a radius of 3 nm ~ 10 nm. These pores are filled in an environment where the concrete is stored between 60% and 90% relative humidity. Stockhausen et al. [53] use Differential Thermal Analysis (DTA) on the cement stone's freezing point of gel water is about -43°C.
- (4) Adsorbed water: A layer of about one to two and a half water molecules adsorbed on the solid surface, filling in pores with a radius of about 1.5 nm. The freezing point of this component is currently the subject of mixed conclusions. According to the results of DTA analysis by Stockhausen et al. [53],

adsorbed water does not undergo phase change in the range of -160°C. In contrast, studies by Ubelhack [54] and Zech [55] showed that this water freezes between -60 ~ -130°C.

Stockhausen [56] modified the Kelving equation by considering the effect of the adsorbed water film. The thickness of the adsorbed water film was added to the original equation to give the relationship between the actual pore radius and the freezing point for different pores, as shown in Eq. (15).

$$\begin{cases} \text{Cylinder pores : } r_k = \frac{3.9}{\ln \frac{273.15}{273.15+T}} + 12 \\ \text{Slit pores : } r_k = \frac{3.3}{\ln \frac{273.15}{273.15+T}} + 10 \end{cases} \quad (16)$$

Where r_k is the pore radius (Å), T is the freezing point of the pore solution (°C).

Due to the different freezing points of pore water inside the concrete, capillary effects occur according to the Setzer thermodynamic model. Pore water freezes much below 0°C. As the pore radius decreases, concrete may exist in a state where newly formed ice (e.g., in capillary pores) and liquid water (e.g., in gel pores) exist simultaneously at a specific constant temperature. Because of the different vapour pressures of ice and water, there is a thermodynamic imbalance, and water is transported from the gel pore to the capillary pore. The diameter of the capillaries is large, so the water here freezes immediately. As a result, the volume of ice in the capillary pore and the pressure of ice on the surrounding pore walls increase despite the constant temperature.

Considering the water-ice phase change, the relationship between pore radius and freezing point, and the capillary effect, G. Wiedemann [52] proposed a pore model, as shown in Fig. 9. The model describes the variation in the internal pores of concrete at low temperatures and the effect of the pore-water phase change on the strength at low temperatures. It assumes that the concrete is saturated with water and divides the cooling process into five temperature stages.

The first temperature stage is from 20°C to 0°C, all the pores are filled with water, and there is no phase change in this temperature range, the concrete specimens will shrink during cooling.

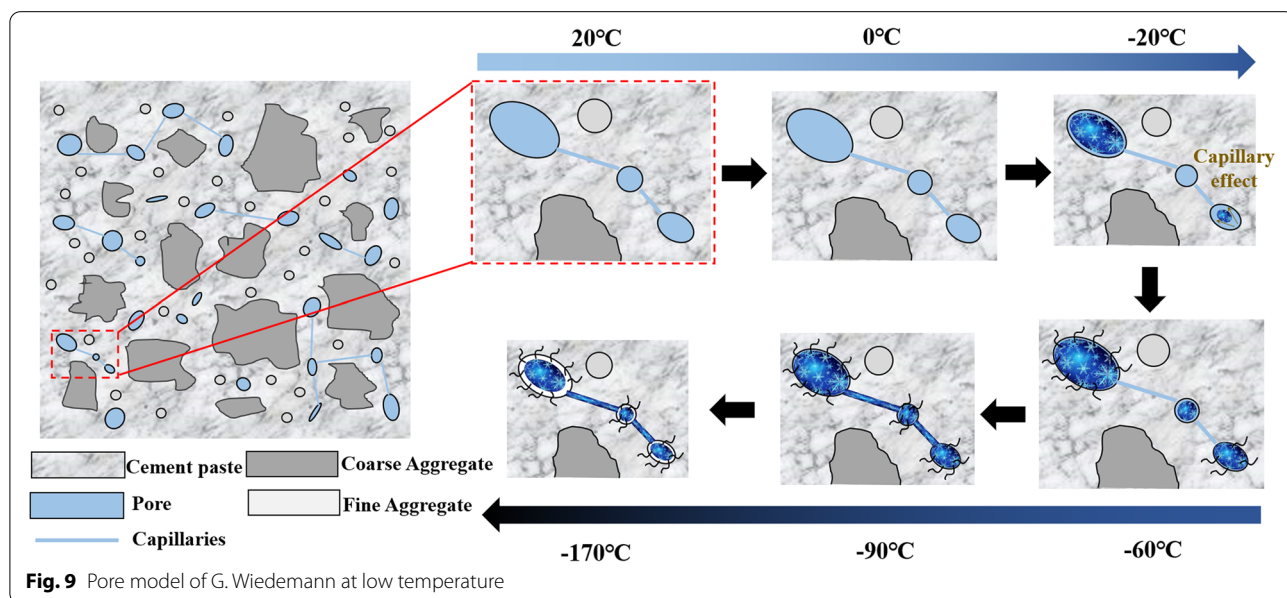
The second temperature stage is from 0°C to -20°C. When the temperature is below 0°C, the water in the larger pores starts to freeze, and the excess water will be pushed into the surrounding pores. With further cooling of the ice, the ice shrinks more because its coefficient of thermal expansion is greater than that of the cement matrix. Also, because the vapour pressure of water is slightly higher than the vapour pressure of ice at the same temperature, a gap is formed between the ice and the pore wall into which water from other pores can diffuse. Since the ice exerts no or very little pressure on the pore walls, shrinkage occurs mainly in that temperature range. The compressive strength increases with the ice continuously filling up the larger pores.

The third temperature stage is from -20°C to -60°C. In water-saturated concrete, when the temperature is below -20°C, the larger pores will be filled with ice. Ice forms in the smaller pores as the temperature decreases further, impeding water flow. As a result of the 9% volume

expansion occurring when water changes from the liquid phase to the solid phase. Therefore, water-saturated concrete expands significantly in this temperature range, and ice exerts a high tension on the matrix, leading to microcracks formation. Due to the ice pressure and the tensile stresses that form cracks, the compressive strength of the concrete grows at a slower rate compared to the second stage.

The fourth temperature stage is from -60°C to -90°C. During this stage, although the capillary effect still attracts water and increases the amount of ice, the water in the smaller pores begins to freeze, slowing or even terminating the capillary effect. With continued cooling, the ice gradually shrinks and breaks away from the pore walls, reducing the pressure of the ice on the pore walls. The ice can carry and transmit some stresses without creating harmful microcracks; thus, the concrete strength continues to increase.

The fifth temperature stage is from -90°C to -170°C, where almost all pore water freezes. The ice continues to shrink and separate from the pore walls, reducing concrete strength. Simultaneously, since the coefficient of thermal expansion of the matrix is higher than that of the aggregate, the shrinkage of the matrix will be more significant, and the matrix will be more compacted with the total (this process occurs in all low-temperature stages). The interface transition zone (ITZ) between aggregate and matrix, where cracks occur at room temperature, is pre-stressed and will retard the increase and development of micro-cracks due to load action. These two opposite



effects will result in a peak strength of concrete at low temperatures.

Conclusion and outlook

This paper reviews the current research results on concrete's mechanical properties at low temperatures. The evolution laws of its compressive strength, tensile strength, flexural strength, elastic modulus, and stress-strain relationship at low temperatures are summarized. The proposed model for predicting the mechanical properties of concrete at low temperatures is given. According to the G. Wiedemann pore model, the changes in the internal structure of concrete at low temperatures have been carefully described, and the mechanism of its mechanical property enhancement has been discussed. The main conclusions obtained are as follows.

- (1) At low temperatures, concrete's compressive, tensile, and flexural strengths increase significantly, and the main factors are temperature and moisture content. As the temperature continuously decreased, the concrete strength increased first and remained stable. The maximum compressive strength occurs around -120°C , the ultimate tensile strength occurs between -30°C and -70°C , and the full flexural strength occurs around -60°C . When the temperature is below -120°C , the strength is only related to the initial moisture content and not the temperature. The Takashi Miura model and the Rostasy & Scheuermann model are also recommended as prediction models for concrete compressive and tensile strength at low temperatures.
- (2) At low temperatures, concrete's axially compressed stress-strain curve changes significantly. As the temperature decreases continuously, the elastic modulus of concrete increases, the peak stress increases, and the peak strain decreases. The concrete stress-strain relationship becomes nearly linear when the temperature below -70°C , and the trend is more evident with higher water content. This paper suggests using Xie's constitutive model as the prediction model of the stress-strain relationship in concrete at low temperatures.
- (3) Considering the water-ice phase change, the relationship between pore radius and freezing point, and the capillary effect, the cooling process is divided into five stages according to the G. Wiedemann pore model.

However, many of these research results come from the late twentieth century, and the conclusions are not

uniform, so much work is still to be accomplished in this field.

- (1) Many kinds of literature are difficult to obtain the original test parameters, the dispersion of test results from different types of literature is large, and the quantitative prediction model is challenging to establish. And the previous studies mainly focused on the effects of moisture content and temperature on the strength of concrete. And less attention has been paid to other factors, such as pore distribution, the relationship between pore size and freezing point, the nature of ice at low temperatures, and low-temperature curing time. All these factors influence concrete's mechanical properties at low and ultra-low temperatures. Further experiments need to be designed to study the mechanical properties of concrete under the coupling effect of multiple factors using controlled variables and orthogonal tests and to establish a strength prediction model influenced by various factors.
- (2) With the development of the science and technology of concrete and the emergence of increasingly complex engineering problems, ordinary concrete can no longer fully meet practical engineering needs. The new cementitious composites, such as strain-hardening cementitious composites (SHCC) and ultra-high-strength cementitious composites (UHPC), have been gradually applied to civil engineering structures in cold regions, and it is still unknown how the mechanical properties of these new concrete change at low and ultra-low temperatures. It is urgent to investigate the effects of fiber type, fiber length, and fiber-matrix interface on the low-temperature properties and obtain the mechanical properties of these new concretes at low temperatures.
- (3) Current research on the mechanical properties of concrete at low temperatures has focused on the quasi-static rate, with less research on the dynamic mechanical behavior. Further attention needs to be paid to the effect of strain rate on the low-temperature properties of concrete, including the total strain rate of low strain rate ($10^{-2} \sim 10^0$), medium strain rate ($10^0 \sim 10^2$), and high strain rate ($10^2 \sim 10^4$). A model for the effect of concrete strain rate at low temperatures is necessary. The result of pore water phase change on the Stefan effect at low temperatures is further investigated, and insight into the enhancement mechanism of the strain rate effect at low temperatures is obtained.
- (4) There is a lack of studies on the effects of pore ice content and ice strength on the low-temperature strength of cementitious materials at different

temperatures. A comprehensive explanation for enhancing the mechanical properties of cementitious materials at low temperatures has not been proposed. Meanwhile, many commonly used room temperature test methods are challenging to work at low temperatures, and new test techniques must be developed to characterize the low-temperature properties of cementitious materials. Test methods such as low-temperature low-field NMR, and differential scanning calorimetry can be used to further study the pore structure, freezing point, and ice crystal formation and changes within the pores.

Studying the development pattern and establishing mechanical prediction models are significant and scientifically valuable for expanding concrete materials in low and ultra-low-temperature applications.

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Availability of data and materials

All data generated or analyzed during this study are included in this article.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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