Research progress and application of negative temperature cementitious materials

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Abstract. This article mainly analyzes the geopolymer cement, composite cementing material, magnesium phosphate cement and sulfoaluminate cement suitable for negative temperature environment, and summarizes the different research results at this stage. Finally, some problems that still exist in negative temperature cementitious materials are described.

1. Introduction
The high-cold and high-altitude regions and polar regions have a large number of natural resources such as minerals, oil and gas, and infrastructure construction is required for resource exploration and exploitation in the above-mentioned regions. Cement-based cementitious materials have become a key raw material in my country’s infrastructure construction and have an irreplaceable role. However, the harsh natural conditions in high-cold and high-altitude areas and polar regions make conventional cement-based cementitious materials unsuitable for this area. This incompatibility is specifically manifested in the slow or non-condensing of cement-based cementitious materials, and the slow development of strength or even no strength, which is mainly caused by the negative temperature environment. Conventional cement-based cementitious materials do not participate in the cement hydration reaction due to the freezing of moisture at an ambient temperature below 0 °C, resulting in cement pastes that do not solidify and have no strength.

At present, the construction of cement and concrete under negative temperature environment mainly adopts physical methods such as water and aggregate preheating, surface covering of thermal insulation materials, and laying of warm shed heating piles to ensure cement hydration. However, such methods are cumbersome and subject to many restrictions when applied. Therefore, a large number of scholars have studied the low-temperature and negative-temperature properties of various cementitious materials, in order to realize that when the cementitious materials are directly mixed, poured, and cured on site under negative temperature conditions, their strength development has no or little impact. At present, domestic and foreign scholars have focused on geopolymer cement, composite cementing materials, magnesium phosphate cement and sulphoaluminate cement on cementing materials under negative temperature environments.

2. Geopolymer cement
Zhao Meijie and Yu Junnan of Harbin Institute of Technology have studied the performance of alkali-activated slag cementitious materials under negative temperature environment [1,2]. Zhao Meijie used
water glass and sodium hydroxide as the alkali activator to discuss the strength development of alkali-activated slag mortar after being formed under the constant negative temperature environment of -5 ℃, -10 ℃ and -20 ℃, and used ordinary silicate. Cement and silica fume replace part of the slag to modify the alkali-activated slag. The results show that: the lower the temperature, the smaller the compressive and flexural strength of the alkali-activated slag mortar; Under the curing temperature of -20 ℃, the compressive strength of the mortar reaches 11.91 MPa for 1 d, which is 60% of the 28 d compressive strength. The strength of the mortar is mainly developed in the early stage; Both cement and silica fume promote the strength development of alkali-activated slag mortar.

Yu Junnan prepared high ductility mortar by mixing PE fiber in alkali-activated slag mortar, and adding steel fiber to modify it. The mechanical properties and volume of the mortar under constant negative temperature environment curing at -5℃ and -10℃ were studied. The results show that the compressive strength of PE fiber reinforced alkali-stimulated slag mortar is more sensitive to temperature. At a curing temperature of -10 ℃, the compressive strength of the mortar at 28 days reaches 30.17% of the standard curing. The addition of PE fiber enhances the volume stability of the mortar. The addition of steel fiber significantly improves the strength of the mortar.

Ye Jiayuan et al. studied the alkali-excitied bauxite beneficiation tailings mortar formed at low temperature (1 ℃), and the curing conditions in the temperature range of -13 ℃~17 ℃ affect the strength of the mortar [3]. The results show that this curing environment with alternating positive and negative temperatures will delay the setting and hardening of the mortar, but the strength of the mortar will continue to develop steadily with the curing age.

3. Composite cementitious material

There are two main types of composite cementitious materials: the composite of different cements and the composite of cement and a large amount of mineral admixtures.

Dai Guoxin et al. studied the mechanical behavior of phosphoaluminate-Portland composite cement paste under -2 ℃, -10 ℃, and -18 ℃ environmental curing [4]. The results show that the addition of phosphoaluminate cement can significantly improve the negative temperature mechanical properties of Portland cement.

Kong Yulong et al. prepared a pipe grouting material suitable for use in an environment of -5 ℃ [5]. The cementing system of this squeeze material is composed of Portland cement, sulfoaluminate cement, gypsum, slag, and fly ash. By adding additives such as lithium carbonate, calcium formate, defoamer, etc., the 1 d compressive strength can reach 23.25 MPa.

Lanzhou Jiaotong University has conducted a lot of researches on the negative temperature performance of Portland cement-mineral admixture composite cementitious materials under the curing condition of -3 ℃ [6,7]. Among them, Lou Xuyu et al. studied the influence of fly ash on the strength and pore structure of low-alkali cement concrete under the condition of -3 ℃ curing. The results show that the activity of fly ash is inhibited in a negative temperature environment. After adding fly coal, the pore size distribution of concrete is optimized, but the compressive strength is reduced. Li Yao studied the macro-mechanical properties and hydration characteristics of Portland cement-silica fume composite cementitious materials under environmental curing at -5 ℃ and -10 ℃. The results show that the negative temperature mechanical properties of the composite cementitious material mixed with silica fume are improved. The negative temperature curing conditions did not change the hydration product composition of the composite cementing material, but inhibited the progress of hydration.

Shenyang Jianzhu University has conducted a lot of research on the negative temperature performance of Portland cement-mineral admixture composite cementitious materials under -10 ℃ curing conditions [8,9]. Among them, Zhang Yahui studied the influence of silica fume content on the 3 d, 7 d, 28 d compressive strength of concrete under constant negative temperature (-10 ℃) curing after 4 hours of pre-curing. The results show that when the content of silica fume is 10%, the compressive strength of concrete is the best, and the compressive strength of 3 d reaches 22.4 MPa. Wang Ning studied the hydration characteristics and mechanical properties of Portland cement-blast
furnace slag composite cementitious materials under -10 ℃ curing conditions. The results show that the accelerated hydration period of the composite cementing material is delayed, and the flexural and compressive strength of the composite cementing material mortar decreases.

4. Magnesium Phosphate Cement

Wang Hongtao successfully prepared fast-hardening and high-strength magnesium phosphate cement. The strength development law of the magnesium phosphate cement mortar cured at -10 ℃, -20 ℃ and -30 ℃ after molding for 25 minutes was studied [10]. The results show that: under the curing condition of -20 ℃, the compressive strength of magnesium phosphate cement mortar in 1 h is still greater than 10 MPa, and the compressive strength in 3 h can reach 17 MPa.

Pei Liqiao and Dai Min studied the magnesium phosphate cement paste and mortar cured at -15 ℃ with ethylene glycol solution as the liquid component and the effect of glycol solution concentration, borax content and water-cement ratio on its performance [11,12]. The results show that: under the curing condition of -15 ℃, when the performance of the magnesium phosphate cement paste is the best, the 2 h compressive strength is greater than 15 MPa. When the performance of magnesium phosphate cement mortar is the best, the 2 h compressive strength is greater than 20 MPa.

Tao Qi et al. studied the mechanical strength of the molded magnesium phosphate cement concrete under the conditions of -10 ℃, -15 ℃, and -20 ℃ [13]. The results show that: under the condition of -10 ℃ curing, the 28-day compressive strength of magnesium phosphate cement concrete is greater than 60 MPa, and the flexural strength reaches 7.2 MPa.

Jia Xingwen et al. increased the system temperature by adding bauxite, using phosphoric acid and methyl cellulose as antifreeze and water-retaining components, respectively, and prepared a magnesium phosphate cement suitable for emergency repair at -20 ℃. The compressive strength can reach 20-40 MPa in 2h at -20 ℃ [14].

5. Sulphoaluminate cement

Deng Junan et al. found that sulfoaluminate early-strength cement has delayed hydration at -5 ℃, but its strength can still develop. At -10 ℃, adding a small amount of calcium nitrite as an antifreeze, the 28d compressive strength of mortar and concrete can reach 30 MPa [15].

Ding Xiuzhi found that the hydration and hardening speed of sulfoaluminate cement is still fast under the environment of 0 ℃. Under the condition of constant temperature of -5 ℃, with a small amount of admixtures, early-strength concrete can still be configured, and the 3 d compressive strength is greater than 20 MPa [16].

Wang Jingyu and Ye Jiayuan of the China Building Materials Research Institute summarized and analyzed the hydration, performance and application of sulfoaluminate cement under low temperature conditions [17-19]. Use sulfoaluminate cement clinker and anhydrous gypsum to make sulfoaluminate cement for experiment at -10 ℃ and -20 ℃. The effects of antifreeze, retarder, and early strength agent on the hydration characteristics of sulfoaluminate cement at negative temperature and the strength of cement paste produced at negative temperature are also studied. The results show that sulphoaluminate cement has broad application prospects in winter construction projects, infrastructure construction in severe cold areas, and rapid repair in low temperature environments. Under negative temperature conditions, calcium chloride has the best effect as an antifreeze. Under the condition of -10 ℃, when the content of anhydrous gypsum is 15%, the self-made sulphoaluminate cement has the best performance. At -20 ℃, when the anhydrous gypsum content is 5%, the self-made sulphoaluminate cement has the best performance. At -10 ℃, 0.6% borax has the best retarding effect on self-made sulfoaluminate cement, and the 3d compressive strength of the cement paste reaches 38.8 MPa. At -20 ℃, 0.6% lithium carbonate has the best effect on promoting the early strength of self-made sulfoaluminate cement, and the 3d compressive strength of the cement paste reaches 9.7 MPa.
6. Other cementitious materials

Sinopec Petroleum Engineering Technology Research Institute has conducted certain research on cementing cement suitable for polar cold sea areas. Among them, Liu Haoya, Bao Hongzhi, Zhao Wei, etc. used modified high alumina cement as the cementing material, antifreeze coagulant solution as the liquid component, and added an appropriate amount of alcohol-ammonia coagulant and setting time regulator, equipped with negative temperature cementing slurry, and studied its mechanical properties and hydration micro process at -18 °C [20-22]. The results show that the cement paste can be hardened at -18 °C for 0.5 to 3 hours, and its compressive strength can reach 3.5 to 9 MPa in 24 hours. The hydration degree of cement paste is lower than that at room temperature, but the ettringite content in the hydrated product is higher than that at room temperature. Zhao Jintuan et al. used TK-G-4 type low negative temperature grouting material to complete the winter construction task of pipeline grouting [23]. When this grouting material is used at an ambient temperature of 0~5 °C, the 1 d compressive strength can reach 38.0 MPa. When used at an ambient temperature of -5~10 °C, the 1 d compressive strength can reach 37.8 MPa.

7. Conclusion

In general, the research and development of negative temperature cementitious materials can help solve the construction problems in high-cold and high-altitude areas and polar regions, and has broad market prospects. Many scholars have conducted a series of studies on negative temperature cementitious materials and have achieved certain results, but there are also some problems. Therefore, it is necessary to improve the raw material selection of negative temperature cementing materials, reduce the types of admixtures in the raw materials, and develop ultra-low temperature (below -20°C) negative temperature cementing materials that can be used in construction environments, and improve its stability, economy and applicability.

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