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Fundemental study on the properties of cement grout using lithium nitrite

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ABSTRACT

When grout freezes in the post-tensioning concrete of cold weather, there is a possibility that cracks may occur in PC steel direction of concrete member due to the freezing expansion of grout. Therefore, the recommendation for design and construction of grout in Japan is not to grout in cold weather with a daily mean temperature of 4℃ or less. There are many cases where grouting in cold weather must be avoided, and this problem is a major obstacle in year-round construction.

In this study, the authors aim to develop a non-freezing cement grout without heat curing in cold weather. The fluidity and the strength development of grout using lithium nitrite in a low-temperature environment were examined. A full-scale modeling test using concrete member was examined to clarify the fulling and strength development under actual winter conditions. As a result, it was confirmed that grout using lithium nitrite has a good strength development in a low-temperature environment. And in the full scale modeling test, there was no problem in filling the grout into the sheath, and the compressive strength was higher than standard grout.

KEYWORDS: *cement grout, cold weather construction, lithium nitrite, strength development, fluidity*

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1. INTRODUCTION

There are two main roles for grouting the ducts of post-tensioned concrete members. One is to provide efficient bond between the pre-stressed steel bar and the concrete member. The other is to prevent corrosion of the pre-stressed steel bar. It is important to conduct complete filling of the void spaces within the duct to fulfill these roles. On the other hand, when constructing cold-weather cement grout, there is a possibility that the cracks may occur in the direction of pre-stressing the steel bar due to the freezing expansion of cement grout **[1]**. Therefore, the recommendation for design and construction of grout in Japan **[2]** is not to grout in cold weather with a daily mean temperature of 4°C or less. When filling grout in cold weather, it is necessary to construct a large curing shed for heat curing to prevent freezing of grout. As a result, the fuel cost of the heater increases. For that reason, there are many cases where grouting in cold weather must be avoided, and this problem is a major obstacle in the year-round construction.

It is necessary to develop a non-freezing cement grout in cold-weather to solve this problem. When improving cold resistance and strength development of cementitious materials, a nitrite and nitrate-based accelerator are commonly used **[3]**. Lithium nitrite ($LiNO_2$, called LN) is widely known to contribute to cold resistance and initial strength development **[4]**, and also used as cement-based repair materials that exhibit an anti-rust effect for steel materials. Additionally, it is also known that the effect of the LN replacement on the fluidity of cementitious materials is relatively small **[5][6]**.

In this study, the authors aim to develop a non-freezing cement grout without heat curing in a low temperature environment of –10 °C or less. The fluidity and the strength tests of the grout using LN in a low temperature environment were conducted in order to confirm the performance of cement grout, and a full-scale modeling test under actual winter condition was conducted to clarify the basic properties of the cement grout using LN such as the filling and strength development.

2. BASIC PROPERTIES OF CEMENT PASTE USING LITHIUM NITRITE

2.1 Outline of the experiment

In this chapter, the compressive strength, hydration heat, and pore structure change over time of cement paste using LN were measured in order to confirm the strength development at low temperature by LN.

2.2 Materials used and mix proportions

Normal Portland cement (C, density : 3.16 g/cm^3) was used, and a material containing LN as a main component was used as the accelerator. The water-to-cement ratio (W/C) was 43% with reference to the general cement grout mixuture**[2]**. The replacement ratios of LN were 0, 2, 4, and 6% of the unit weight content of cement.

2.3 Test method

When grouting in the cold weather, it is necessary to keep the temperature of grout at 5°C or more for 3 days of material age in principle **[2].** When it is susceptible to freezing and thawing in cold weather, it is recommended to secure a casting temperature of concrete at about 10 °C by the Standard Specifications for Concrete Structures in Japan **[7]**. In this experiment, the temperature of the materials was controlled in a temperature- and humidity-controlled testing room (10 ± 1 °C and 85% ± 5% relative humidity) and the mixing was performed in the same room using a hand mixer. After mixing, the paste was poured into a φ50 × 100 mm lightweight mold, the casting surface was covered with a thin vinyl sheet. After that, the specimens were cured in a constant temperature chamber at -5 °C. The compressive strength (JSCE-G 531) was measured at each age (3, 7, 14 and 28 days). A thermocouple in φ100 × 200 lightweight mold were set to measure the temperature history, and the temperature of the specimen was measured immediately after the casting. The pore diameter and the pore volume of cement paste were measured using mercury intrusion porosimetry (MIP). The specimens for MIP were sampled about 5 mm square from the center of the φ50 × 100 mm specimen. Initially, the specimens were immersed for 4 hours in acetone to stop hydration. Later, the specimens were dried in a vacuum desiccator.

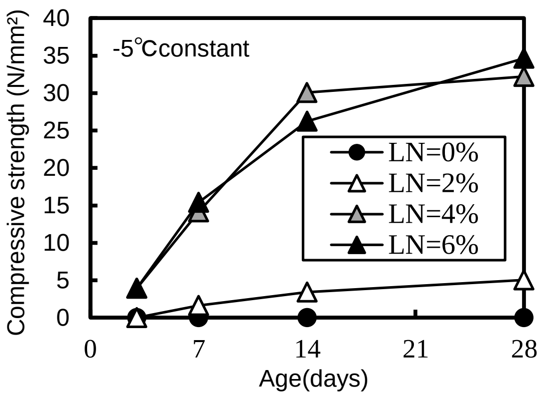

Fig.1 Compressive strength

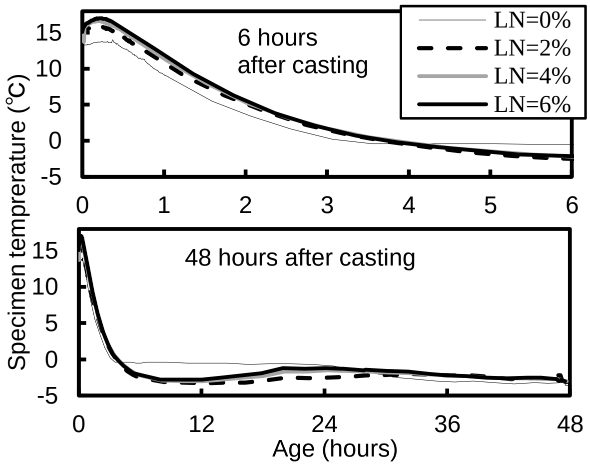

Fig.2 Temperature history of the specimen

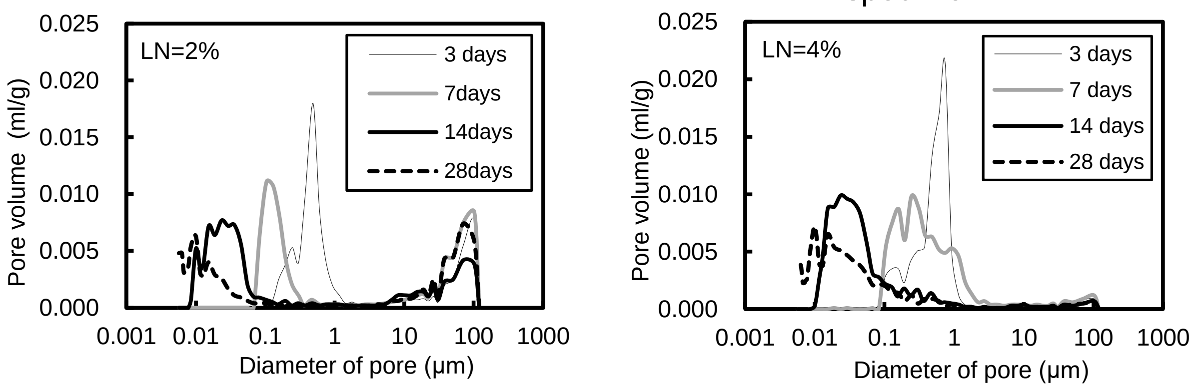

Fig.3 MIP

2.4 *Experimental results and discussion*

Fig.1 shows the results of compressive strength, and Fig. 2 shows the temperature history of the center of the specimen immediately after casting. In the case of LN-free

(LN = 0%), the compressive strength was not measured because the specimens were not hardened at all ages and the specimens broke during the demolding stage. And in the case of LN = 2% at 3 days of material age, the compressive strength was also not measured because the end of the specimen was damaged during demolding. On the other hand, in the case of LN=2% after 7 days, strength development was confirmed. However, the compressive strength at 28 days is 5.1N/mm^2. It is considered that the strength development was delayed due to the effect of initial frost damage. Whereas, in the case of LN = 4% and LN = 6% at 3 days, strength development was confirmed, and the strength of LN=4% and LN=6% at 28 days was 32.2 N/mm^2 and 34.7 N/mm^2, respectively. The temperature history of LN = 0% in Fig. 2 dropped rapidly after casting. And then the temperature remained constant at a value of about 0 ° C. After that the temperature tended to drop again. It is considered that this is due to the latent heat, which indicates freezing of cement grout. On the other hand, the temperature peak of adding LN immediately after casting is higher than that of LN-free. Also, the temperature tended to rise again from about 12 hours after casting. It is known that Nitrite ion (NO_2^-) promotes hydration of C_3S and C_2S in cement, and reacts with C_3A in cement to nitrite type hydrate ($3CaO \cdot Al_2O_3 \cdot Ca(NO_2)_2 \cdot 10H_2O$)**[8][9]**. For this reason, it is considered that the temperature peak changes and good initial strength development of adding LN were obtained.

Fig. 3 shows the pore dimeter distribution of LN = 2% and LN = 4%. In the case of LN=4%, the peak of the pore dimeter distribution in the range of 0.1-1 μm shifts to the finer diameter side as the material ages. On the other hand, in the case of LN=2%, the peak of the distribution was confirmed in the range of 10-100 μm at 3 days of material age, and the peak was also confirmed in the same range at each age. This is presumed to be due to the effect of initial frost damage.

3. QUALITY EVALUTION OF CEMENT GROUT USING LITHIUM NITRITE

3.1 Outline of the experiment

On the basis of the results of Chapter 2, the fluidity and the change of compressive strength of cement grout using LN were examined in a low temperature environment.

3.2 Materials used

Normal Portland cement (C, density: 3.16 g/cm^3) was used and a material containing LN as a main component was used as the accelerator. In addition, high viscosity admixture of the expanding- and bleeding- free (Ad, main component: melamine sulfonic acid compound, water-soluble polymer ether compound) with reference to the recommendation for design and construction of grout in Japan **[2]** was used.

3.3 Test method

Table-1 shows the experimental factors. The water-to-cement (W/C) ratio of cement grout was 43%. The ratio was determined by test mixing to ensure the fluidity of high viscosity type grout (JP funnel flow time: 14-23 seconds) **[2]**. The replacement ratios of LN were 0-12% of the unit weight content of cement on the basis of the results in Chapter 2 and the previous study **[4][5][6]**. The mixing and fluidity test of grout were performed in a temperature- and humidity-controlled testing room (10 ± 1 °C and 85% ±

5% relative humidity), to control the temperature of the grout. A fluidity test according to JSCE-F 531 was performed in the same room by using a JP funnel (outflow pipe length:30mm). The flow time of the grout was measured after 0, 15 and 30 min of mixing. After the fluidity test, grout specimens for compressive strength (φ50 x 100 mm) were cast, and the test surface of the specimens were covered with a thin vinyl sheet to protect the grout by sealed curing. After casting, the specimens were cured at a constant temperature of -5℃, -10℃ and -15℃ until the predetermined test age. The compressive strength (JSCE-G 531) was measured after 7 and 28 days of curing at each temperature condition. After 28 days of curing, some specimens were additionally cured at a constant temperature of 20℃ for 28 days in order to confirm the strength recovery after low temperature curing for 28 days. In this study, the target range for the flow time was 14-23 seconds, and the target value of compressive strength after 28 days was 30 N/mm^2 or more on the basis of the recommendation for design and construction of grout in Japan **[2]**.

Table1. Experimental factor

Factor		Specification
Cement grout	Water-to-cement ratio (W/C)	43.0 %
	Replacement ratio of LN	0-12 %
	Replacement ratio of Ad	1.0 %
Curing condition		-5° C, -10° C, -15° C (until 28 days of material age) ↓ After that, +20° C (until 56 days)
Mesurement item		Flow time (JP funnel flow test)
		Compressive strength

3.4 EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 4 shows the relationship between the flow time and the replacement ratio of LN. The area surrounded by the gray color in the figure 4 is shown as the target range **[2]** for the flow time of high viscosity type grout. In the case of the LN replacement ratio of 0-7%, the flow times immediately after mixing were similar. However, when the LN replacement ratio exceeded 8%, the flow time increased. Furthermore, the flow time after 15 and 30 minutes increased when the LN replacement ratio exceeded 8%. When the LN replacement ratio was 12%, the flow time could not be measured because the fluidity of grout was lowered remarkably. It is considered that the nitrite ion (NO_2^-) contained in LN promoted the hydration reaction of cement **[8][9]**, with an increase of LN replacement ratio. Therefore, it is thought that the LN replacement ratio should be set to 10 % or less in order to satisfy the target range of flow time.

Fig. 5～7 shows the relationship between the compressive strength and the LN replacement ratio. The bold line in Fig. 5～7 indicates 30N/mm^2, which is the standard specification **[2]** of compressive strength for grout. In each case, when the LN replacement ratio was in the low range, the strength was very small. In these cases, a frozen pattern was founded on the surface of the specimen before the test. In addition, the strength development was delayed even after 28 and 56 days of curing. Therefore, it is considered that the initial frost damage occurred in these replacement ranges. On the other hand, when the LN replacement ratio increased, the compressive strength increased remarkably.

In the case of curing at -5 ℃ and -10℃, the range of the LN replacement ratio satisfying the target value of compressive strength was 3-5% and 4.5-8%, respectively. On the other hand, in the case of curing at -15℃, the compressive strength at 28 days was lower than target value (30 N/mm^2) regardless of the LN replacement ratio. However, after additional curing at a constant temperature of 20 ℃ for 28 days, the compressive strength of LN replacement ratio of 7% or more was larger than target value.

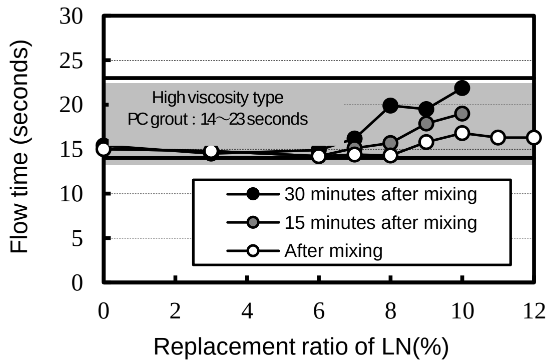

Fig.4 Fluidity time

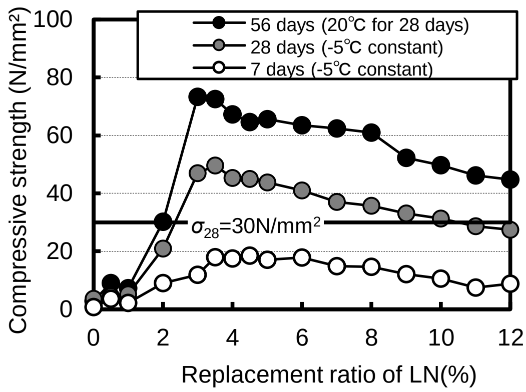

Fig.5 Compressive strength (-5° C)

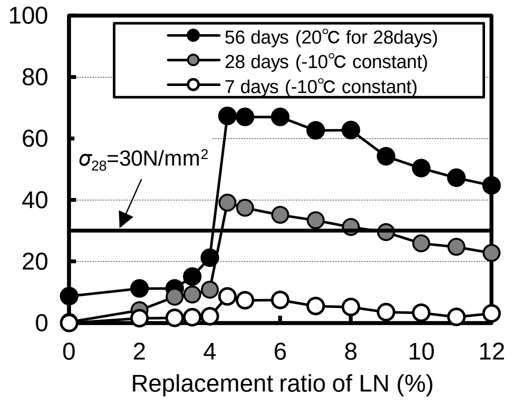

Fig.6 Compressive strength (-10° C)

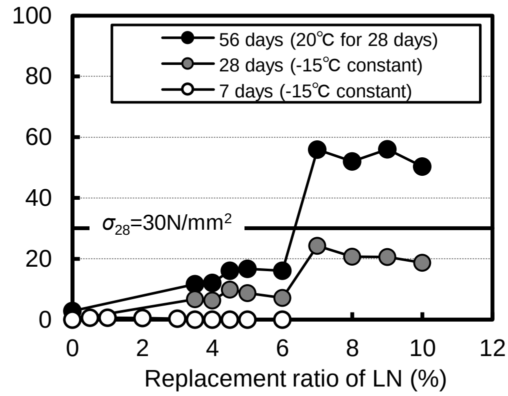

Fig.7 Compressive strength (-15° C)

4. FULL SCALE MODELING TEST USING CONCRETE MEMBER

4.1 Outline of the experiment

From the results of Chapter 2 and 3, it was confirmed that the cement grout using LN had good strength development in a low temperature environment. On the basis of the results of the experiment, a full scale modeling test using a sheath tube was examined to clarify the fulling and strength development under actual winter condition, and the various evaluation tests based on the recommendation for design and construction of grout in Japan **[2]** were conducted.

4.2 Full scale modeling test specimen

Fig. 8 shows the outline of the full scale modeling test specimen using a sheath tube, and Fig. 9 shows the shapes of the sheath tube and pre-stressed steel wire. The specimens were fabricated on the basis of the construction manual for PC Grout & Pre-Grout PC Steel in Japan **[10]**. The horizontal length of the sheath was 30.7 m. The upslope and downslope were 10 degrees, and the height difference was 1.1 m. In order to confirm the filling of the cement grout in the sheath by visual observation, transparent polyethylene sheath tube with an inner diameter of 81 mm and pre-stressed steel wire with a nominal diameter of 15.2 mm were used.

4.3 Test method

Table 2 shows the experimental factors. The materials used are the same in the previous chapter. The water-to-cement ratio (W/C) was determined by test mixing in order to satisfy the specified value **[2]** for the flow time. In the case of normal grout, the LN replacement ratio was free (LN=0%), and heat curing was performed by jet heater in a curing shed in order to maintenance a temperature of 5-10 ° C until 3 days of material age. On the other hand, in the case of non-freezing grout, the LN replacement ratio of cement grout was 5%, and heat curing was not performed. However, the specimen was covered with a snow protection sheet in order to prevent damage of the sheath tube by snow loading.

Fig. 10 shows the history of daily mean temperature during the experiment (Kitami City, Hokkaido). The test was conducted from February to May, and the outside temperature during the grouting test was approximately -10 ° C.
The material for cement grout and grout mixer pump were cured in a curing shed with a temperature of about 5-10 ° C. The cement grout was also mixed in the same curing shed.

4.4 Measurement item

The various evaluation tests were conducted on the basis of the recommendation for design and construction of grout in Japan **[2]** as follows: 1)flowability test of grout for prestressing bar (JSCE-F 531), 2)material separation resistance test for grout for pre-stressed bar (JSCE-F 534), 3) bleeding ratio and expansion ratio test of grout for pre-stressed bar (JSCE-F 535). The grout specimens for compressive strength (φ50 x 100 mm) were cast immediately after mixing (before grouting). After that, the casting surface of the specimen was covered with a thin vinlyl sheet. The compressive strength (JSCE-G 531) was measured at each age (7, 28 and 91 days). In the case of normal grout (LN=0%), some specimens for compressive strength were also cured in the snow protection sheet without heat-curing.

4.5 Experimental results and discussion

Table 3 shows the results of tests for cement grout. In both cases, all test results satisfied the standard value of grout **[2]**. It was confirmed that the grout could be filled into the sheath tube completely. Fig. 11 shows the results of the compressive strength. In the case of normal grout (LN=0%) without heat curing, the strength development was remarkably delayed, and the strength at 28 days of material age was about 20N/mm^2. On the other hand, the strength development was similar for non-freezing grout (LN=5%) and normal grout (LN=0%) with heat curing, and the strength of LN=5% at 28 days was about 48 N/mm^2. It was confirmed that the strength development satisfied the standard value of grout (30 N / mm^2 or more from 7 days to 28 days).

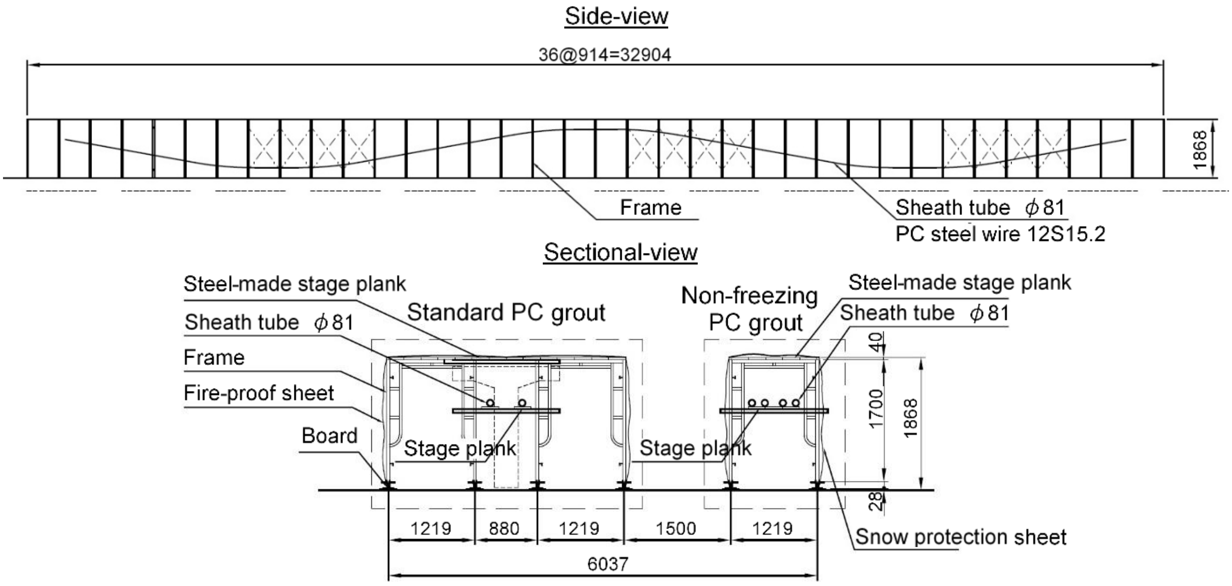

Fig.8 Outline of the full scale modeling test specimen

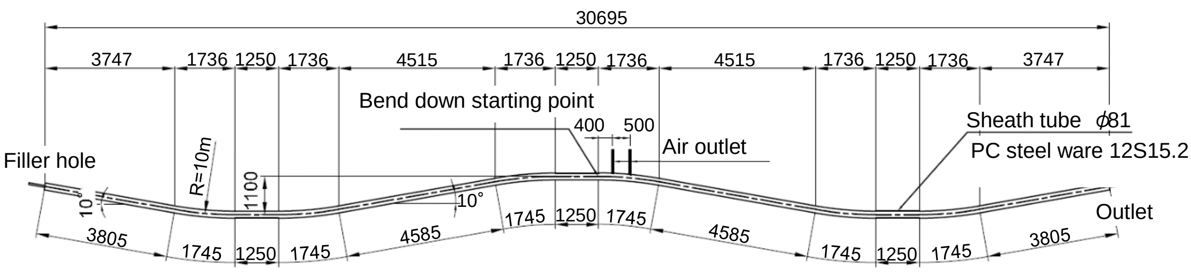

Fig.9 Shapes of the sheath tube and pre-stressed steel wire

Table2. Experimental factors

Case	Curing condition	Target fluidity time	W/C	Measurement item
Normal grout (LN=0%)	Curing shed + heat curing	14-23 seconds (high viscosity type PC grout)	41.5 %	Fluidity Material separation resistance Bleeding ratio Expansion ratio Compressive strength
Nonfreezing grout LN=5%	No curing		42.5 %	

Table3. Results of quality standard tests for grout

Measurement item	Test method	Standard	LN=0%	LN=5%
Fluidity(JP funnel)	JSCE-F 531	14-23 seconds	22.8 seconds	15.7 seconds
Material separation resistance	JSCE-F 541	Not bleeding	Not bleeding	Not bleeding
Bleeding ratio	JSCE-F 535	0.3 % or less	0.0 %	0.0 %
Expansion ratio		-0.5-0.5 %	0.0 %	-0.3 %

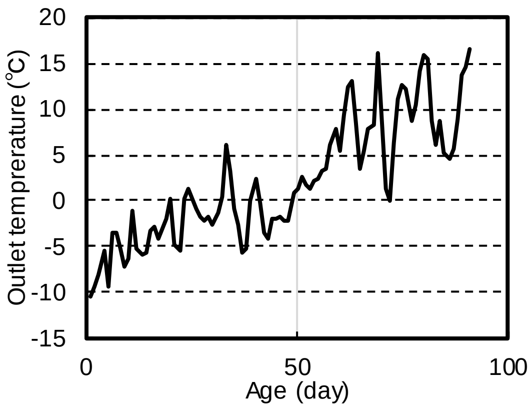

Fig.10 History of daily mean temperature (Kitami City, Hokkaido)

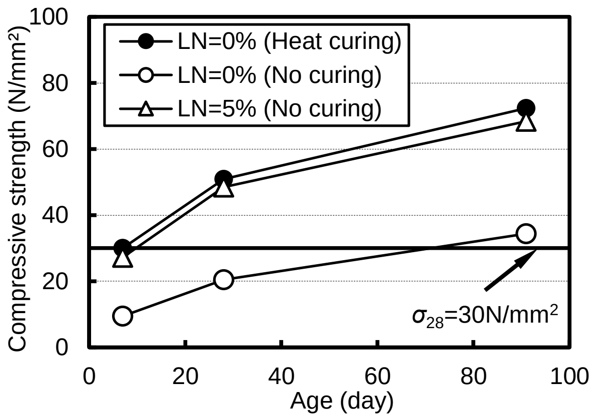

Fig.11 Compressive strength

5. CONCLUSIONS

In this study, the authors aim to develop a non-freezing cement grout without heat curing in cold weather. The fluidity and the strength development of the cement grout using lithium nitrite in a low-temperature environment were examined. And the full scale modeling test using a sheath tube was examined to clarify the fulling and strength development under actual winter condition. The results of the study are summarized below.

1) In the case of LN replacement ratio of 0-7%, the effect of LN replacement ratio on the flow time is relatively small. However, in the case of a LN replacement ratio of 8% or more, the flow time after 15-30 minutes tended to be longer.
2) In the case of low temperature curing at -5° C and -10° C, the initial frost damage could be prevented by adding an appropriate replacement of LN to grout, and the compressive strength was 30 N/mm^2 or more at 28 days of material age.
3) From a full-scale modeling test using sheath tube, it was confirmed that the grout could be filled into the sheath tube completely and all test results satisfied the standard value of grout.

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