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NANO2-NASO4 COMBINED ADDITIVE IN COLD CONCRETE.(U)
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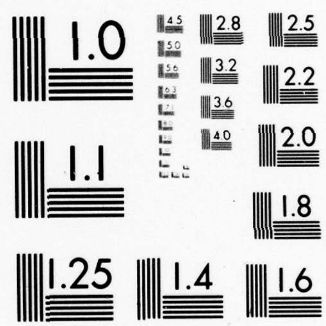

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May 1979

$NaNO_2$-$NaSO_4$ COMBINED ADDITIVE IN COLD CONCRETE

UNITED STATES ARMY
CORPS OF ENGINEERS
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE, U.S.A.

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Experiments were conducted in which $NaNO_2$, Na_2SO_4 and $N(C_2H_4OH)_3$ were added to cold concrete to prevent freezing and promote strengthening. $NaNO_2$ was added in an amount equal to 13.3% of the water content of the concrete, and Na_2SO_4 and $N(C_2H_4OH)_3$ in amounts equal to 3% and 0.03%, respectively, of the cement content. The concrete was kept from freezing at -10°C and the strength increased to over 60% of the design strength after 28 days and 80%-90% of the design strength after three months. If this type of additive is used under positive temperature conditions (+10 to +15°C), it results →

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20. Abstract (cont'd.)

in an early strengthening effect, good concrete density, resistance to infiltration of up to 28-30 kg/cm^2, strength in the later stages 5 to 10% greater than that of ordinary concrete and physical properties superior to those of ordinary concrete. Because of the rust-preventing action of $NaNO_2$, the cold concrete additives do not have any rusting or corroding effects on the steel bars. The facts that cold concrete is convenient to work with, that the additives can be obtained easily and that the costs are comparatively low make this a method that is well worth adopting and using widely in carrying out construction during winter.

<u>Table of Contents</u>

1. Introduction

In the northern regions of our nation, there are from several to over 6 months each year during which cold temperature conditions prevail and during which time progress on basic construction work and the scale of operations are greatly limited. Since the establishment of the nation, under the guidance of Chairman Mao's revolutionary line, we have adopted various methods for winter construction on the battlefront of basic construction and have amassed definite practical experience concerning it. Of these, cold concrete mixed with chlorates has been widely used in industrial, civil construction, harbor, railroad and bridge construction projects and in mine construction. However, because of interference and sabotage attributable to the counterrevolutionary revisionist line of Liu Shaoqi and of the influence of the doctrine of slavish imitation of the West, the problem of rusting and corrosion of steel bars in cold concrete containing chlorates was not solved and the method ceased to be used.

Under the impetus of the Great Proletarian Cultural Revolution, the workers, cadres and scientific research personnel of our institute, with class struggle as our guide, resolutely supported the Party Line, carried out open-door management of scientific research, and, "breaking away from foreign models, took our own independent course of industrial development." In order to develop a cold concrete hardening additive suited to conditions in our nation, we engaged in experimental research work and proposed using $NaNO_2$ as an antifreeze agent in an $NaNO_2$-Na_2SO_4 combined additive for cold concrete. Good results were obtained when this was put into use.

This paper represents a summary of the results of several years of experimental work. Because of our low level of ideological awareness and technical skill, we would welcome the criticisms and corrections of our comrades in respect to points of inadequacy in our work.

2. Basic Theory of Hardening of Cold Concrete

The major factor affecting construction with concrete during winter is temperature. We have no control over natural changes in atmospheric temperature. The best that we can do is to prevent or diminish the freezing of the water in the concrete by scientific means on the basis of changes in atmospheric temperature in order to maintain a liquid phase and thus facilitate continuous hardening of the concrete.

Water freezes at 0° C. However, when any soluble substance is added to water, the vapor pressure of the solution is decreased, with the result that the freezing point of the solution is lowered. According to Lavoisier's law, the temperature at which ice begins to separate out (freezing point) in an aqueous solution of electrolytes is directly proportional to concentration and inversely proportional to the molecular weight of the solute. It is also related to the number of ions and the degree of dissociation.

This becomes even more evident when a graph of the temperature components of a simple binary (water - $NaNO_2$) system is used to study the process of the freezing of water in an aqueous solution of $NaNO_2$ on the basis of physicochemical theory. If we assume that the original concentration of the solution is lower than the concentration of the eutectic temperature correspondance (i.e., the antifreeze agent is dissolved in the water with a large amount of water and a small amount of solvent), and if we do not consider supercooling of the solution, then the relationship between freezing temperature and weight concentration is as indicated in Figure 1.

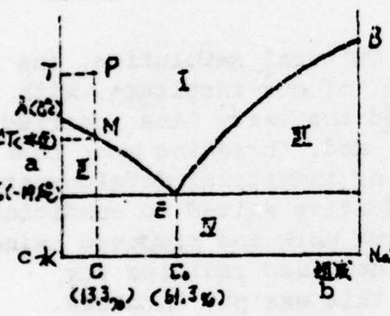

Figure 1. Graph of Temperature Components of Water-$NaNO_2$ System

a) Freezing point
b) Component
c) Water

For example, the original concentration of the $NaNO_2$ solution is C and the temperature is T. The coordinates of the graph meet at point P (T,C). Because the heat of the solution is dissipated, the temperature decreases. When the temperature decreases to the freezing point ΔT (coordinates at M) of the solution, ice begins to separate out from the solution. If the temperature continues to fall, the quantity of ice separating out increases, the quantity of water decreases, the concentration of the solution increases and the freezing point of the solution decreases further. The coordinates of the solution in the temperature component graph move along the curve AE. At this time, each temperature of the solution corresponds to a single component (or concentration). Each concentration corresponds to a single freezing point. When the temperature has decreased to a certain point, i.e., to point E (at the corresponding temperature T_e and the corresponding equilibrium concentration C_e), the solvent (water) and the solute together form a solid solution which separates out. Point E is the minimum eutectic point of this system and T_e is the minimum eutectic temperature of the solution. The results of measurements and the data both confirm that the minimum eutectic temperature of $NaNO_2$ is -19.6° C. C_e is the minimum eutectic cpncentration of the solution. When the temperature of the solution is higher than the freezing point ΔT of the solution, ice does not separate out (the coordinates being in region I of the graph). When the temperature is lower than the minimum eutectic temperature E, all of the water in the solution goes into solid phase and separates out (region IV). When the temperature falls between the freezing point ΔT and the minimum eutectic temperature E, the water in the center of the solution forms into ice and separates out, while the remainder of the water stays in the liquid phase (region II and region III).

On the basis of the preceding analysis, the physicochemical characteristics of freezing of the water in cold concrete and of the water in ordinary concrete are obviously different, the freezing temperature of the water in cold concrete having to be far lower than that at which pure water freezes. In addition, the concentration of the solution in the cold concrete is not a constant. As the atmospheric temperature decreases, the concentration of the solution undergoes corresponding changes and the freezing point also gradually decreases. On the basis of the minimum eutectic temperature of $NaNO_2$, -19.6° C, the cold concrete can harden within a range within -19.6° C. However, when the quantity of $NaNO_2$ mixed in exceeds the amount of water used in the concrete by 13.3%, the development of strength is greatly retarded, and, when it exceeds the amount of water used by 33.5%, at -15° C, 7 days are required for condensation. This is not satisfactory in actual construction work. Thus, it is necessary to control the content suitably on the basis of the laws for increasing strength and to confirm the range of the hardening temperatures. For this reason, controlling the freezing point of the solution in the concrete to between -8° C and 8.5° C, thus assuring that most of the water will remain in the liquid phase and allowing a small amount of it to freeze, is the basis for the capacity of cold concrete containing $NaNO_2$-Na_2SO_4 combined additive to promote continuous hardening without freezing damage at conditions under -10° C.

3. Research on $NaNO_2$-Na_2SO_4 Combined Additive

(1) Materials used in the experiments

1. Cement: No. 500 ordinary silicate cement produced in Harbin.

2. **Sand:** Medium river sand.

3. **Rock:** 1-3 cm river current rock.

4. **$NaNO_2$:** HG-526-67 second grade. See Table 1 for indices. External appearance: Light yellow white crystals.

5. **Na_2SO_4:** HG-520-67 2nd or 3rd grades for use in ordinary cement. 1st grade for prestressed concrete. See Table 2 for indices. External appearance: White, homogeneous fine grains. Na_2SO_4 containing water of crystallization should be converted to anhydrous Na_2SO_4.

a)指 标 名 称	b)指 标
$NaNO_2$ (以 c 计) %≥	98
$NaNO_3$ (以 c 计) %≤	1·9
水不溶物 d)	e) 不规定

Table 1

a) Index designation
b) Index
c) (calculated on dry base)
d) Matter not soluble in water
e) Not specified

a)指 标 名 称	b)指 标		
	c)	d)	e)
Na_2SO_4 %≥	98	95	92
NaCl %≤	0·7	1·5	1·8

Table 2

a) Index designation
b) Index
c) 1st grade
d) 2nd grade
e) 3rd grade

6. Triethanolamine, $N(C_2H_4OH)_3$: Colorless or light yellow oily substance exhibiting high alakinity and readily soluble in water.

(2) The action of $NaNO_2$ in cement and concrete

1. Effectiveness of $NaNO_2$ in lowering the freezing point

In order to ascertain its effectiveness in lowering the freezing point, we used the thermal analysis method to determine the freezing points of aqueous solutions and concrete containing differing amounts of $NaNO_2$. The results of the determinations are shown in Table 3 and Table 4.

As can be seen from a comparison of Table 3 and Table 4, $NaNO_2$ is more effective in lowering the freezing point of concrete than it is in lowering the freezing point in aqueous solutions. This is because $NaNO_2$, Na_2SO_4 and such hydroxides as $Ca(OH)_2$ have a synergic effect in the liquid phase of concrete.

Thus, under conditions of -10° C, when fixed amounts of $NaNO_2$ are added during the mixing of concrete, it is possible to assure that the concrete will not undergo freezing. When the liquid phase in the concrete reaches the freezing ppint at this time, a small amount of water is allowed to freeze. However, this does not damage the structure of the concrete and it continues to increase in strength. The quantity of $NaNO_2$ to be used,,i.e., the optimum amounts to be mixed in under fixed cold conditions, is closely related to the design strength of the concrete, the water-ash ratio, the type of cement, the amount of cement used and the maintenance cold temperature.

2. The plasticizing action of $NaNO_2$ on cement and concrete

The plasticizing action of $NaNO_2$ can be discussed from the following four standpoints. The experiments were conducted at +15° C.

(1) Effects of $NaNO_2$ on cement condensation time

As can be seen from Table 5, $NaNO_2$ had very great effects on cement condensation time, with condensation time constantly growing longer as the quantity added was increased. When it was combined with Na_2SO_4, condensation time was also very long.

	a) 100克水中含盐类的克数									b) 析出固溶体时	
	2	4	6	8	10	15	20	25	30	c) 克／100克水	d) 温度°C
$NaNO_2$	—0·9	—1·8	—2·7	—3·6	—4·5	—6·0	—6·9	—7·8	—8·9	61·3	—19·6
NaCl	—1·2	—2·4	—3·5	—4·8	—6·0	—9·3	—12·7	—16·0	—21·2	30·1	—21·2

Table 3. Freezing Points of Aqueous Solutions of NaCl and $NaNO_2$ in Degrees C

- a) Number of grams of salt in 100 g of water
- b) At time of separated solid solution
- c) g/100 g of water
- d) Temperature °C

a) 标号/配合比	b) 相对水溶液的浓度%/占水泥重%					
c) 哈产矿渣500°水泥						
400° / 0·45:1:1·295:3·18	11·1 / 5	13·3 / 6	15、5 / 7	17·7 / 8	20 / 9	0 / 0
d) 冰点（℃）	−6·29	−6·6	−7·83	−7·65	−7·65	−0·377
200° / 0·6:1:2·2:4·72	5 / 3	10 / 6	11·6 / 7	13、3 / 8	15 / 9	16·6 / 10
d) 冰点（℃）	−3·79	−6·57	−7·16	−7·51	−8·88	−9·15
e) 哈产普通500°水泥						
400° / 0·45:1:1·295:3·18	8·85 / 4	13·3 / 6	—	—	—	0 / 0
d) 冰点（℃）	−5·12	−3·63				−0·43
200° / 0·6:1:2·2:4·72	5 / 3	10 / 6	13·3 / 8	—	—	0 / 0
d) 冰点（℃）	−3·79	−6·59	−8·46			−0·32

Table 4. Effects of $NaNO_2$ on Freezing Point of Concrete

a) Marker number/compounding ratio
b) Relative concentration of aqueous solution(%)/cement weight(%)
c) Slag 500# cement produced in Harbin
d) Freezing point (°C)
e) Ordinary 500# cement produced in Harbin

a) 外加剂占水泥重%			b) 水灰比	初凝 c) 时：分	终凝 d) 时：分	初~终 e) 时：分
$NaNO_2$	Na_2SO_4	$N(C_2H_4OH)$				
0	0	0	0.26	4:27	7:53	3:28
6	0	0	0.26	7:00	9:22	2:22
8	0	0	0.26	8:19·	12:32	4:13
0	3	0	0.26	4:00	6:55	2:55
6	3	0	0.26	6:22	9:26	3:04
6	3	0·03	0.26	6:20	11:[illegible]0	5:10
8	·3	0	0.26	6:23	11:45	5:22
8	3	0·03	0·2	10:25	—	—

Table 5. Effects of $NaNO_2$ on Cement Condensation Time

a) % by weight of additive in cement
b) Water-ash ratio
c) Initial condensation
hours : minutes
d) Final condensation
hours : minutes
e) Initial - final
hours : minutes

(2) Effects of $NaNO_2$ on standard consistency of cement

Cement mortar containing 6 to 8% of $NaNO_2$ has very high fluidity at standard consistency. The experiments shown in Table 6 indicate that $NaNO_2$ not only prolongs condensation time but that it also has a good water-decreasing effect. At standard consistency, water is decreased by 10 to 15% as compared to blank cement mortar. This serves to decrease the amount of water used in cold concrete and provides conditions for increasing strength.

a) $NaNO_2$占水泥重(%)	b) 标准稠度用水量	c) 减水量(%)	d) 测定温度(℃)
0	0·245	0	10
6	0·216	11·8	10
8	0·208	15·1	10

Table 6. Effects of $NaNO_2$ on Standard Consistency of Cement

a) Weight (%) of NaO_2 in cement
b) Quantity of water used for standard consistency
c) Amount of decrease in water (%)
d) Determination temperature (°C)

(3) Effects of $NaNO_2$ on plastic strength of cement

In order further to clarify the effects of $NaNO_2$ on the process of hardening of cement, we used the needle penetration method to determine the plastic strength of the $NaNO_2$. The magnitude of the value for plastic strength, i.e., initial condensation strength, indicates the characteristics of hardening of the water - cement - $NaNO_2$ system from the time mixing is begun up to before final condensation. From the relationship between strength and condensation time it is possible to obtain numerical reference data for selecting the quantity of $NaNO_2$ to be mixed in and for assuring pouring time.

As can be seen from Figure 2, an $NaNO_2$ content of less than 2% does not have any effect on plastic strength. However, when the amount added is increased, plastic strength gradually decreases and condensation time is constantly prolonged. The pastic strength equilibrium stages in the

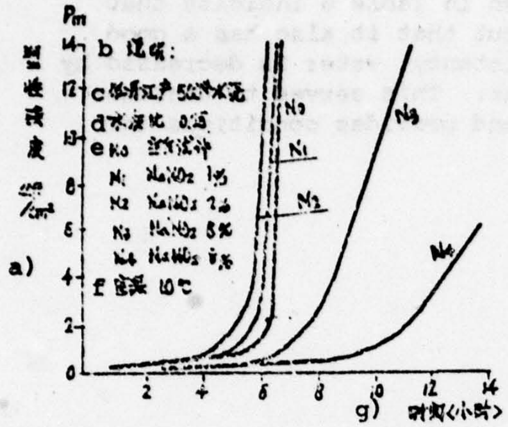

Figure 2. Effects of $NaNO_2$ on Plastic Strength of Concrete

- a) Plastic **strength, kg/cm^2**
- b) **Explanation**
- c) **500# cement produced at [2 characters illegible] jiang.**
- d) **Water-ash ratio, 0.25**
- e) **N_0 [poorly legible]**
- f) **[poorly legible] 10° C**
- g) **Time (hours)**

figure indicate that the cement particles **undergo comparatively rapid physical and chemical dispersing effects, during which time the rate of hydration of the aluminates in the minerals of the cement is retarded. In addition, the liquefying action of C_3A** hydrates **on $NaNO_2$ increases the active surface of the cement particles and at the same time decreases the quantity of minerals that have** not **reacted with the water. This is extremely beneficial to the formation of cement rock. As the result, the compactness of the concrete is greatly increased. This is confirmed by the marked increase in the marker number for resistance to infiltration. Consequently, it does not have an unfavorable effect on the properties of cold concrete.**

(4) **<u>Effects of $NaNO_2$ on the degree of collapse of the concrete</u>**

The tests shown **in Table 7 indicate that $NaNO_2$ has marked effects on both the water-ash ratio and degree of collapse of concrete. Under conditions of similar compounding ratios, $NaNO_2$ with a water content of 13.3% mixed into**

a) 混凝土标号	b) 配合比	c) $NaNO_2$对水泥重%	d) 坍落度 (cm)	e) 工作度 (秒)	f) 温度 (℃)
g) 400号	0·4:1:1·295:3·18	0	0	28″	10
〃	0·4:1:1·295:3·18	5·34	2	10″	10
〃	0·5:1:1·295:3·18	0	2	—	10
〃	0·5:1:1·295:3·18	6·66	5	4″	10
〃	0·55:1:1·295:3·18	0	4·3	—	10
〃	0·55:1:1·295:3·18	7·3	—	—	10
h) 200号	0·55:1:2·2:4·72	0	0	22″	10
〃	0·55:1:2·2:4·72	7·33	0·5	19″	10
〃	0·65:1:2·2:4·72	0	0	10″	10
〃	0·65:1:2·2:4·72	8·66	3	4″	10
〃	0·7:1:2·2:4·72	0	3	5″	10
〃	0·7:1:2·2:4·72	9·33	8	1·8″	10

Table 7. Effects of $NaNO_2$ on the Degree of Collapse of Concrete

a) Concrete number
b) Compounding ratio
c) % by weight of $NaNO_2$ in cement
d) Degree of collapse (cm)
e) Degree of work (seconds)
f) Temperature (°C)
g) No. 400
h) No. 200

the concrete can decrease the water-ash ratio to 0.05, i.e., a decrease in the amount of water used of about 10%. If the water-ash ratio does not change, the degree of collapse can increase 3 to 3 cm and can even increase to over 10 cm. This serves to decrease the amount of water used in carrying out winter construction with cold concrete and also provides the conditions for sufficient mixing and pounding time.

By means of the foregoing tests, it was possible to ascertain on a preliminary basis that $NaNO_2$ is a comparatively good antifreeze agent and that it is also an agent for reducing water content and retarding condensation, thus having a definite plasticizing action on concrete.

(3) Dose selection of $NaNO_2$-Na_2SO_4 combined additive

1. Dose selection of $NaNO_2$

The proper amount of $NaNO_2$ to be mixed into concrete is determined by testing both at positive and negative temperatures. In the tests, the $NaNO_2$ is first dissolved in water, and, according to different dose concentrations, concrete with water-ash ratios of 0·45 and 0·6 are compounded. After it has undergone artificial mixing, shaking and formation, separate samples are maintained under standard conditions at normal temperature and in a freezing room at -10° C. Compression strength was determined for different periods of cooling and was compared with that of ordinary concrete. Table 8 shows the test results. The following points can be ascertained from the test results.

(1) Under conditions of +10 to +15° C, an $NaNO_2$ content of less than 5% by weight of the cement has a definite early strengthening effect. When the water-ash ratio is 0·45 and when the $NaNO_2$ content is 5% by weight of the cement, strength 110.8% that in the blank samples can be achieved in 3 days. However, after 14 days, the development of strength slows and an early-strengthening effect is not evident as the quantity of $NaNO_2$ mixed in is increased. By the 28th day, there is a comparatively great loss of strength.

(2) Under conditions of -10° C, an $NaNO_2$ content of 6% by weight of the cement when the water-ash ratio is 0·45 results in some slowing of strength in 3 days, with fairly rapid development of strength after 7 days. By the 28th day, strength reaches more than 60% of that in the blank tests. An $NaNO_2$ content of 8% by weight of the cement when the water-ash ratio is 0·6 is comparatively effective, with strength reaching 50 to 60% of that in blank samples by 28 days. This indicates that it is suitable to use $NaNO_2$ as an antifreeze agent with water in the amount of 13.3% concrete compounded of ordinary silicate cement under conditions of -10° C, that this combination can prevent early freezing of the concrete and at the same time can contribute to continuous increase in its strength. If the amount of $NaNO_2$ mixed in is not sufficient, the freezing point does not decrease sufficiently and damage due to freezing can then be sustained. Addition of excess amounts of $NaNO_2$ is not beneficial to strength in later stages.

% by weight of $NaNO_2$ in cement	Compression strength (kg/cm²)							
	Maintenance at positive temperature				Maintenance at -10° C			
	3 days	7 days	14 days	28 days	7 days	14 days	28 days	3 months
400# concrete, compounding ratio 0.45 : 1 : 1.295 : 3.18								
0	81·2 / 100	130·2 / 100	295 / 100	282·7 / 100	215·3 / 100	271 / 100	308·7 / 100	321 / 100
5	90 / 110·8	184·3 / 102·3	263·5 / 89·3	227·3 / 80·4	45 / 20·9	97 / 35·8	173 / 56	231·1 / 71·9
6	75·7 / 93·2	152·5 / 84·6	247·3 / 83·8	236·6 / 83·7	38·7 / 17·9	108·7 / 40·1	198 / 64·1	252·5 / 78·6
7	75·7 / 93·2	152·2 / 84·6	253·7 / 86	173·3 / 57·4	39 / 18·1	103·7 / 38·3	179 / 57·9	240·3 / 74·8
8	75·3 / 92·7	170·2 / 94·5	239·3 / 81·1	207·3 / 73·3	30·3 / 14·1	82·7 / 30·5	171 / 55·4	233·2 / 72·6
9	64·5 / 79·4	150·4 / 83·5	220·7 / 74·8	203·7 / 73·8	13·6 / 6·3	63·3 / 23·4	142 / 45·9	189·3 / 58·9
200# concrete, compounding ratio 0.6 : 1 : 2.2 : 4.72								
0	43·8 / 100	—	144·3 / 100	177 / 100	131 / 100	164 / 100	194·3 / 100	228·7 / 100
7	47·8 / 109·1	—	147 / 101·8	187 / 105.6	11·9 / 9·1	35·3 / 21·5	94 / 48·4	125·1 / 54·7
8	41·5 / 94·7	—	133·7 / 92·7	172 / 97·2	16·7 / 12·7	60 / 36·5	110 / 56·6	132 / 57·7
9	44·7 / 102·1	—	139·3 / 96·5	171 / 96·6	7·4 / 5·6	41 / 25	95 / 48·9	136·6 / 59·7
10	38·3 / 87·4	—	125 / 86·6	152 / 85·9	18·3 / 14·3	56·3 / 34·3	96 / 49·4	143·4 / 62·7

Note: In the maintenance at 10° C columns, the blank test values are standard maintenance strengths.

Table 8. $NaNO_2$ Dose Selection Tests

2. <u>Tests combining $NaNO_2$ with Na_2SO_4, NaCl, $CaCl_2$ and NaF</u>

As can be ascertained from the preceding discussion, $NaNO_2$ has the defects of delaying cement condensation time and lowering strength at 28 days. For these reasons, we had to search for an early-strengthening agent, which when combined with $NaNO_2$, would achieve the following results: Be able to provide a good early-strengthening effect in the early stages; promote rapid growth of strength at negative temperatures; contribute to rapid growth in strength after change to positive temperatures; give a loss of strength in the later stages not exceeding 10%. We selected the following substances for these tests.

Na_2SO_4 (optimum mixture quantity is 3%)

NaCl, $BaCl_2$ (amounts to be added limited to an allowable range of 1 - 2%)

NaF (optimum mixture quantity, 1.7%)

$N(C_2H_4OH)_3$ (optimum mixture quantity, 0.55%)

Each of these substances was combined with 6% of $NaNO_2$ and comparisons were made of their conditions at -10° C, of percentages of blank sample strength reached in 28 days and of percentages of loss of strength after change to positive temperature. Table 9 shows the results. The results obtained from these combinations indicate the following points.

(1) Combining $NaNO_2$ with Na_2SO_4 produced the best results. Strength was comparatively high after 28 days at -10° C and loss of strength after 1 year and 6 months did not exceed 10%.

(2) Single combinations of NaCl, $CaCl_2$ and NaF with $NaNO_2$ produced poor results in all cases. However, comparatively good results were obtained when they were combined with Na_2SO_4 at the same time. The best results were obtained with NaF, with strength after 28 days at -10° C reaching 47% of blank strength and with almost no loss of strength after 1 year and 6 months. In consideration of convenience of operations, it is disadvantageous for a combination additive to be too complicated. Therefore, we did not use combinations consisting of more than three types of additives with $NaNO_2$. Although NaCl and $CaCl_2$ were of definite effectiveness, their effects were not particularly evident when they were combined singly with $NaNO_2$. Moreover, it is not advantageous to use them since they further the danger of corrosion and rusting of steel bars. Combination of NaF alone with $NaNO_2$ is not of very good effectiveness, while good effects are achieved when it is combined with $NaNO_2$ and Na_2SO_4. However, NaF is highly toxic and costly and is not generally used. If definite protective measures are taken during operations and if the raw materials can be readily obtained, its use can of course be considered.

On the basis of the foregoing results, we decided to use $NaNO_2$ with Na_2SO_4 to compound the combined additive for cold concrete.

% by weight of additive in cement		Compression strength (kg/cm^2)							
		3 days	7 days	14 days	28 days	2 mos	3 mos	5 mos	1 year 6 mos
0	-	59 / 27·1	126 / 58	120 / 82·8	217 / 100				262·2 / 120·8
$NaNO_2$	6		11·9 / 5·5	35.3 / 16·1	90·4 / 41·7		125·1 / 57·6		
$NaNO_2$ Na_2SO_4	6 3	8·4 / 3·9	34.2 / 15·8	92 / 42·4	100·9 / 46·5		135 / 62·2		249 / 114·7
$NaNO_2$ NaCl	6 1	4·6 / 2·1	14·9 / 6·9	74 / 34·1	65·4 / 30·1	83·5 / 38·5	85·8 / 39·5	103·3 / 47·6	215 / 99
$NaNO_2$ NaCl Na_2SO_4	6 1 3	7·4 / 3·4	24·3 / 11·2	96 / 44·2	83·3 / 38·3	103 / 47·4	109 / 50·2	109·3 / 50·2	222·1 / 102·3
$NaNO_2$ $CaCl_2$	6 1·5		1·95 / 0·9	17 / 7·8	41 / 18·8	66·1 / 30·4		86·5 / 39·8	155 / 71·4
$NaNO_2$ $CaCl_2$ Na_2SO_4	6 1·5 3	4·05 / 1·86	20·2 / 9·3	48·8 / 22·4	86 / 39·6	110·6 / 50·9		154 / 70·9	245 / 119
$NaNO_2$ NaF	6 1·7	8·1 / 3·7	9·4 / 4·3	16·5 / 7·6	65 / 30	101 / 46·5	111 / 51	124 / 57	206 / 95
$NaNO_2$ NaF Na_2SO_4	6 1·7 3	5·8 / 2·67	11·5 / 5·3		102 / 47	136 / 62·6		139 / 64	261 / 120

Notes: 1. In the blank tests, standard maintenance was applied. In all other cases, maintenance was at -10° C and the cement contained 0.03% by weight of $N(C_2H_4OH)_3$.

2. In the 1 year 6 month tests, the sample was maintained at -10° C for 5 months, after which it was transferred to maintenance at +10 to +15° C for 13 months.

mos: months

Table 9. Tests of Combinations of Na_2SO_4, NaCl, $CaCl_2$ and NaF With $NaNO_2$

3. Tests of $NaNO_2$ - Na_2SO_4 combined additive

In order to determine a scheme for combining $NaNO_2$ and Na_2SO_4, further studies were conducted of the effects of Na_2SO_4 and triethanolamine in compoundings and of the amounts to be added.

(1) Effects and quantities added of Na_2SO_4

The effects and amounts to be added of Na_2SO_4 were determined by two experiments. First, tests of strength-increasing effects were carried out at positive temperatures with a 1 : 3 cement-concrete mixture having a water-ash ratio of 0.55. After that, it was combined with 6% $NaNO_2$. Then, the strengths of concretes with water-ash ratios of 0·45 were determined for different periods of cold, being maintained at +15° C and at -10° C, in order to facilitate determination of the suitable amounts to be added in.

Table 10 indicates that, at positive temperatures, the addition of Na_2SO_4 alone has evident early-strengthening effects. When the % by weight added was 3%, strength 270% of that under blank conditions was obtained in 3 days, with somewhat greater strength being achieved after 28 days.

% by weight of Na_2SO_4 in cement	Water ash ratio	Compression strength (kg/cm^2) 3 days	7 days	28 days
0	0·55	37	123	220
1	0·55	65	143	242
2	0·55	76	196	232
3	0·55	99	167	225

Table 10. Early-strengthening Effects of Na_2SO_4 at +15° C

Table 11 and Table 12 indicate the following points. When Na_2SO_4 is combined with $NaNO_2$, a quantity of 3% is satisfactory in terms of the strength of the concrete. In 3 days, it is possible to achieve a strength 47% of that at 28 days under blank conditions, an increase of about double. As contrasted with the results of tests of $NaNO_2$ alone at positive temperatures shown in Table 8, losses in strength after 28 days were decreased from 43 - 17% to 11 - 6%.

Marker number / Compounding ratio	% by weight of additive in cement: $NaNO_2$	Na_2SO_4	Trieth	Maint. temp. (°C)	Compression strength (kg/cm^2): 3 days	7 days	14 days	28 days
No. 400 / 0·45:1:1·295:3·18	0	0	0	Stand. maint.	62/22·8	132/48·6	223/82	272/100
	6	1	0·03	—10	8·3/3·03	42·3/15·6	110/40·4	172/63·3
	6	2	0·03	—10	11·8/4·3	47·7/17·5	119/43·7	149/54·7
	6	3	0·03	—10	9·7/3·6	43/15·8	122/44·9	177/65
	6	4	0·03	—10	10·2/3·8	46/10·9	109/40·1	157/57·7
	6	1	0·03	Stand. maint.	108·3/38·9	178·3/65·6	229/84·1	256/94
	6	2	0·03	"	130/47·8	184·7/67·6	223/82	253/93·1
	6	3	0·03	"	129·7/47·7	190/69·8	238/87·5	243/89·3
	6	4	0·03	"	125·7/46·3	171·3/63·1	222/81·5	247/90·8

Table 11. Dose Selection of Sodium Sulfate When Value of $NaNO_2$ was Held Constant

Maint. temp. = Maintenance temperature

Stand. Maint. = Standard maintenance

Trieth = Triethanolamine

Marker number Compounding ratio	% by weight of additive in cement			Maint. temp. (°C)	Compression strength (kg/cm^2)			
	$NaNO_2$	Na_2SO_4	Trieth		7 days	14 days	28 days	3 months
No. 400 0·45:1:1·295:3·18	0	0	0	Stand. maint.	252·5 / 65·2	337 / 87	387·7 / 100	
	6	3	0·03	—10	86·3 / 22·3	153·6 / 39·7	232 / 60	
	7	3	0·03	—10	52·7 / 13·6	112·6 / 29·1	185·7 / 47·8	239·0 / 61·7
	8	3	0·03	—10	64·5 / 16·7	117 / 30·2	199·3 / 51·5	267·5 / 69·2
No. 200 0·6:1:2·2:4·72	0	0	0	Stand. maint.	105·1 / 44·5	136 / 57·6	236 / 100	
	7	3	0·03	—10	19·8 / 8·4	66·7 / 28·2	107 / 45·4	
	8	3	0·03	—10	27·5 / 11·7	95 / 40·2	157 / 66·5	
	9	3	0·03	—10	26·8 / 11·7	75 / 31·3	118 / 50	

Table 12. Dose Selection of Sodium Nitrite When Value of Na_2SO_4 was Held Constant

Maint. temp. = Maintenance temperature

Stand. maint. = Standard maintenance

Trieth. = Triethanolamine

As can be seen by contrast with Table 8, which shows findings at negative temperatures, combining Na_2SO_4 with $NaNO_2$ resulted in earlier strengthening than when $NaNO_2$ alone is used, with a comparative increase in strength at 7 days from 17% to 32.5%. At the same time, at 28 days strength reaches over 60% of that in the blank samples.

From a comprehensive review of Tables 8, 9, 10, 11 and 12, it can be ascertained that the optimum $NaNO_2$ content for cold concrete with a water-ash ratio of 0·45 is 6% and that the optimum $NaNO_2$ content for cold concrete with a water-ash ratio of 0·6 is 8%. The aqueous solution concentrations at these times were about 13.3% and the freezing point values were about -8.5° C. Na_2SO_4 was of very little effectiveness in decreasing the freezing point. When the solution concentration was 2%, the freezing point was -0.6° C, and when the solution concentration was 4%, the freezing point was -1.2° C. From this it can be seen that the $NaNO_2$ is the principal antifreeze agent in cold concrete and that the Na_2SO_4 has a definite early-strengthening effect in cold concrete when a liquid phase is present. As the result, continuous increase in the strength of the concrete can occur when the change is made to maintenance at positive temperature. A content of 2 to 3% is quite suitable.

(2) Effects of $N(C_2H_4OH)_3$

We made a comparative study of the effects of triethanolamine at negative temperatures (-10° C). The results, which are shown in Table 13, indicate the following points. Combining triethanolamine with $NaNO_2$ - Na_2SO_4 at negative temperatures resulted in a definite catalytic effect. At 7 days, strength of concrete with a water-ash ratio of 0·45 could be increased 6% and strength of concrete with a water-ash ratio of 0·6 could be increased about 12%. At 28 days, strength was increased about 5% in both cases. Consequently, it is beneficial to add an amount of triethanolamine of 0.03% by weight of cement to cold concrete. However, if suitable conditions are not present, it need not be added.

% by weight of additive in cement	Maint. temp. (°C)	Compression strength (kg/cm^2)				
		3 days	14 days	28 days	3 months	− 3 months + 1 month
400# concrete, compounding ratio 0.45 : 1 : 1.295 : 3.18						
Blank sample	Stand. maint.	252·5 / 65·2	337 / 87	387·8 / 100		
$NaNO_2$ 6 Na_2SO_4 3	−10	65 / 16·9	135·6 / 39·7	210 / 54·4	239	380
$NaNO_2$ 6 Na_2SO_4 3 $N(C_2H_4OH)_3$ 0·03	−10	86·2 / 22·3	135·6 / 39·7	232 / 60		
200# concrete, compounding ratio 0.6 : 1 : 2.2 : 4.2						
		105 / 50·3	136 / 67	200 / 100		
$NaNO_2$ 8 Na_2SO_4 3	−10	27·5 / 13·7	95 / 47·5	157 / 78·5	226	314
$NaNO_2$ 8 Na_2SO_4 3 $N(C_2H_4OH)_3$ 0·03	−10	55·3 / 25·8	122·7 / 61·5	168 / 83·5	226	314

Table 13. Combination Tests With $N(C_2H_4OH)_3$

Maint. temp. = Maintenance temperature

Stand. maint. = Standard maintenance

4. Characteristics of Strength Development of Cold Concrete

(1) Increase in strength when maintained at −10° C

1. Maintained at −10° C for fixed periods and then maintained at positive temperatures (+10 to +15° C). Item 2 in Table 14 shows the states of increase in strength of cold concrete with a water-ash ratio of 0·45. On the 7th day, strength was 31.9% of that of the blank test sample subjected to standard maintenance and on the 28th day, strength was 66.5% of that of

the blank test sample. When a transition was made to a positive temperature after 3 months, in one month it was possible to attain a strength 74% that of the blank test samples given standard maintenance. Eight months after transition to positive temperature (1-year strength) strength was 93.3% that of the blank test samples given standard maintenance, with loss of strength in the latter phase not exceeding 10%. Item 8 in Table 14 shows the characteristics of strength increase of cold concrete with a water-ash ratio of 0.6. Strength at 3 days was 17.9% that of the blank test samples given standard maintenance, strength at 28 days was 81.5% that of the blank test samples given standard maintenance and strength at 9 months after transition to positive temperature following the 3rd month (1-year strength) was 96% that of the blank test samples given standard maintenance, with loss of strength in the latter period not exceeding 5%.

2. In long-term studies at -10° C, strength at 6 months was found to be more than 70% that of the blank test samples given standard maintenance. As can be seen from Item 3 in Table 14, although the strength of cold concrete kept at -10° C for prolonged periods continues to increase, the increase is slow.

3. Item 4 in Table 14 shows the state of increase in strength found when the test samples were kept for long periods at -10° C and also buried in the earth at depths of 20 to 30 mm. As can be seen, strength at 1 month was 73.5% that of blank test specimens given standard maintenance. Because the test samples were buried in the earth, they were not subjected to the impact of air currents, humidity was constant, the ice in the test samples could not readily sublimate and the liquid phase water could not readily evaporate, factors which were favorable for the occurrence of hydration in the cold concrete. For these reasons, strength was 10 to 20% greater than when the samples were introduced directly into conditions of -10° C.

4. Item 5 in Table 14 shows the state of increase in strength found when the test samples were kept for long periods at -10° C and when the surfaces of the test samples were soaked in 5% sodium methyl silicate. The sodium methyl silicate was a product of the Jilin Industrial Chemicals Institute. The concentration was 20%, and, when it was used, it was prepared as a 5% aqueous solution in which the test samples were soaked When this was done, strength at 1 month reached more than 70% that of the blank test samples given normal maintenance and at 6 months reached 75% that of blank test samples given normal maintenance, the increase in strength thus being almost the same as that obtained for test samples buried in the earth. Sodium methyl silicate is capable of reacting with the $Ca(OH)_2$ that separates out when hydration of the cement occurs, producing intense adsorption and crystallization. The reaction products adhere well to the surface of the concrete and do not dissolve in water and inorganic salts. As the result, imbedded hydrophobic films are formed on the walls of the pores and on the walls of the capillary tubes of the concrete, thus preventing dehydration of the concrete and sublimation of the ice crystals in it and ensuring that the moisture in the concrete will bring about satisfactory hydration of the cement.

Item	Marker number compounding ratio	% by weight of additive in cement			Mnt cond	Compression strength (kg/cm)									
		NaNO₂	Na₂SO₄	Trieth		3 days	7 days	14 days	28 days	2 mos	3 mos	3 mos + 1 m	6 mos	1 year	2 years
1	No. 400 / 0·45:1:1·295:3·18	0	0	0	Stn mnt	137/100	215·7/100	271/100	306/100	312/100	328·3/100	349·3/100		411/100	440/100
2	No. 400 / 0·45:1:1·295:3·18	6	3	0·03	—10℃	18·3/18·3	63·5/31·9	135/49·8	205·3/66·5	223·6/71·6	237·1/72·3	258/73·9		372·5/93·3	396·7/90·2
3	No. 400 / 0·45:1:1·295:3·18	6	3	0·03	—10℃				205·3/66·5	223·6/71·6	237·1/72·3	238/72·3	246		305/69·3
4	No. 400 / 0·45:1:1·295:3·18	6	3	0·03	A				225·3/73·5	253·6/81·3	257·1/78·3	266/76·2	265·6		396·7/90·2
5	No. 400 / 0·45:1:1·295:3·18	6	3	0·03	B				215·7/70·4	225·6/72·1	243·5/74·1	261/74·7	261·7		393·3/89·4
6	No. 400 / 0·45:1:1·295:3·18	6	3	0·03	Stn mnt	142/103·8	215/99·8	244/90	279.3/91·4	304·5/97·7	315/94			424·5/103·5	391·7/89
7	No. 200 / 0·6:1:2·2:4·72	0	0	0	Stn mnt	77/100	131/100	164/100	194·3/100	197·3/100	236/100			249/100	355/100
8	No. 200 / 0·6:1:2·2:4·72	8	3	0·03	—10℃	13·8/17·9	55·3/42·2	122·7/74·7	168/81·5		183·3/77·5			239/95	288·3/81·2
9	No. 200 / ·6:1:2·2:4·72	8	3	0·03	Stn mnt	129/167·5	132/100·7	171/104·2	204·3/105·3	225·3/114·1	247/104·7			253·3/101·6	335/94·4

Note: Items 2 and 8 were maintained at -10° C for 3 months, after which they were maintained at +10 to +15° C. Items 3, 4 and 5 were maintained for long periods at -10° C.

Trieth = Triethanolamine; Mnt cond = Maintenance conditions; mos = months; m = month

Stn mnt = Standard maintenance; A = -10° C, buried in earth; B = -10° C, immersed in sodium silicate

Table 14. States of Growth in Strength of Cold Concrete

(2) Increase in strength under maintenance at positive temperature

The test results are shown in Items 6 and 9 in Table 14. Three-day strength of cold concrete with a water-ash ratio of 0.45 was 103.8% that of the blank test samples and at 28 days strength was 91.4% that of the blank test samples. At one year, it was 103.5% that of the blank test samples. Three-day strength of cold concrete with a water-ash ratio of 0.6 was 167.5% that of the blank test samples. At 28 days, it was 105.3% and at 1 year it was 101.6%.

When cold concrete is maintained at positive temperatures the plasticizing action of the $NaNO_2$ causes increase in the denseness of the concrete and the strengthening action of the Na_2SO_4 and $N(C_2H_4OH)_3$ not only gives a very high compression strength but also results in physical and mechanical properties far superior to those of the blank test samples. Resistance to infiltration in particular was better than that in concrete containing $FeCl_3$. At a water pressure of 30, this type of concrete did not have any rusting or corroding effects on steel bars.

(3) Effects of maintenance temperature and time on growth of strength

1. Table 15 shows the effects of different maintenance temperatures on the growth of strength of cold concrete. As can be seen, at 3 days there is an essentially linear relationship between strength and temperature, with strength increasing rapidly as temperature rises and increasing more slowly as temperature decreases.

2. The higher the early-stage maintenance temperature is and the longer it is maintained, the more rapid will be the growth of strength of cold concrete. Maintenance of normal temperature for a fixed period in the early stages is of extremely great significance for the strength of concrete. In actual operations, this can be achieved by raising the temperature of the mixture or by adding a covering after pouring. Table 16 shows the effects of early-stage maintenance temperature and time on the strength of cold concrete.

% by weight of additive in cement	Maint temp (°C)	Compression strength (kg/cm^2)				
		3 days	7 days	14 days	28 days	- 2 months + 1 month
Blank sample	+ 14	56·3 / 25·6	122 / 51·5	162 / 73·8	219 / 100	243 / 111
$NaNO_2$ 8, Na_2SO_4 3, $N(C_2H_4OH)_3$ 0·03	+ 14	69·7 / 31·7	113 / 50·3	141·5 / 64·3	171 / 78	239 / 109
"	+ 8	62 / 28·3	114 / 50·4	141·5 / 64·3	171 / 78	236 / 107·5
"	+ 3 ~ + 7	48 / 28·8	112 / 50·2	147 / 47	189·6 / 88·3	238 / 108·5
"	0 ~ + 1	27 / 12·3	80 / 36·4	138 / 63	160 / 72·9	228 / 104
"	−6	66 / 3	44·5 / 20·3	117 / 53·3	149 / 67·9	249 / 114
"	−10	3·3 / 1·5	23 / 10·5	47·5 / 21·6	89 / 40·5	239 / 109
"	−13 ~ −1	0 / 0	11 / 5	51 / 23·2	91·6 / 41·6	136 / 62

Note: 200# concrete, compounding ratio, 0.6 : 1 : 2.2 : 4.72

Maint temp = Maintenance temperature

Table 15. Effects of Different Maintenance Temperatures on Growth of Strength

% by weight of additive in cement	Maintenance temperature (°C)	Compression strength (kg/cm^2)							
		1 day	3 days	5 days	7 days	14 days	28 days	- 3 mos	- 3 mos + 2 mos
Blank sample	+14		43·8 / 24·7	·		144·3 / 80·5	177 / 100		
$NaNO_2$ 3, Na_2SO_4 3, $N(C_2H_4OH)_3$ 00·3	+14				109·1 / 61·6		117·6 / 97		
"	A	1·25 / 0·71					68·3 / 38·5	100 / 51·3	151 / 85·1
"	B		14·8 / 8·4				90 / 51	142 / 80·5	224·5 / 128
"	C			30 / 16·9			97 / 55	148 / 83·7	218·5 / 124·5
"	D				62·2 / 35·1		106·6 / 60	150 / 58	265·5 / 151·5
"	E					87 / 49·1	117 / 66	156 / 88	255 / 146
"	F				30 / 16.9	66 / 37·3	108 / 60	173 / 97·7	210·7 / 120

Note: 200# concrete, compounding ratio, 0.6 : 1 : 2.2 : 4.72

mos = months

Table 16. Effects of Early-Stage Maintenance Temperature on Growth of Strength

A: -3, one day
-10, 3 months
transfer to
positive temperature

B: -3, 3 days
-10, 3 months
transfer to
positive temperature

C: -3, 5 days
-10, 3 months
transfer to
positive temperature

D: -3, 7 days
-10, 3 months
transfer to
positive temperature

E: -3, 14 days
-10, 3 months
transfer to
positive temperature

F: -3, 28 days
-10, 3 months
transfer to
positive temperature

(4) Effects of differing water-ash ratios on strength

The water-ash ratio had extremely great effects on the strength of cold concrete. Each increase in the water-ash ratio of 0·05 resulted in a decrease in strength of 30 to 40%. The 28-day strength of concrete with a water-ash ratio of 0·4 was over 60% that of the blank test samples, the 28-day strength of concrete with a water-ash ratio of 0·5 was about 50% that of the blank test samples and the 28-day strength of concrete with a water-ash ratio of 0.55 was only about 30% that of the blank test samples. Thus, it can be seen that the water-ash ratio has very great effects. If the water-ash ratio is too great and the original amount of $NaNO_2$ is added, then freezing damage will occur at -10° C. If the quantity of antifreeze agent added is increased, this not only adds to the expense but also may have deleterious effects on the physical and mechanical properties of the concrete.

For this reason, when cold concrete is being mixed, the water-ash ratio should be rigorously controlled and the plasticizing action of the $NaNO_2$ must be taken into full consideration. As low a water-ash ratio should be used consistent with assuring easy workability. Table 17 shows the effects of differing water-ash ratios on the strength of cold concrete.

(5) Frozen strength of cold concrete

From our study of the development of strength of cold concrete, we discovered that although its early strength was comparatively low its frozen strength was comparatively high. The reason for this was that, when $NaNO_2$ with a water content of 13.3% was used, the freezing point fell to -8 to -8.5° C, the difference between this temperature and the maintenance temperature of -10° C (-2 to -1.5° C) resulting in a small amount of freezing. In order to ascertain whether frozen strength of cold concrete could be utilized in construction under fixed conditions, we conducted tests in regard to the characteristics of the frozen strength and the structural strength of cold concrete. No. 200 cold concrete containing differing amounts of $NaNO_2$ was used in the tests.

10 x 10 x 10 cm test samples were formed at positive temperatures immediately after which they were placed in a freezing compartment at -10° C. They were maintained in a cold state for considerable periods, after which they were removed and determinations were made of their frozen strength and of their structural strength after thorough melting. Observations were made of the relationships between these strengths and the quantities of $NaNO_2$ used for differing periods of cold treatment. In addition, determinations were made of the conditions of early stage frozen strength on the basis of the comparative values for frozen strength and structural strength. Table 18 shows the results of the tests of frozen strength and structural strength.

Marker number compounding ratio	% additive NaNO₂	Na₂SO₄	Tri	Compression strength (kg/cm²) Standard maintenance 3 days	7 days	14 dy	28 dy	3 mos	Maintenance at -10° C 3 dy	7 dy	14 dy	28 dy	3 mos	- 3 months + 1 month
No. 400 0·45:1:1·295:3·18	0	0	0	137 / 100	215·3 / 100	271 / 100	308·7 / 100	321 / 100						
No. 400 0·4:1:1·295:3·18				152 / 111	229·3 / 106·4	296 / 109·1	310 / 100·6							
No. 400 0·5:1:1·295:3·18				166 / 121	210 / 97·6	252 / 93	258 / 83·7							
No. 400 0·55:1:1·295:3·18				63·8 / 46·6	188·7 / 87·6	133 / 67·5	225·3 / 73·1							
No. 400 0·4:1:1·295:3·18	5·33	3	)·03	182·3 / 133	231·3 / 107·4	263 / 97·1	301·3 / 97·8		16·3 / 11·9	80 / 39·2	152 / 56·1	206·4 / 64·2	226·4 / 70·5	286
No. 400 0·5:1:1·295:3·18	6·66	3	)·03	166 / 121	210·1 / 97·6	252 / 93	258 / 83·7		10·6 / 7·7	54·3 / 25·3	127 / 46·8	162 / 52·6	185 / 57·6	285
No. 400 0·55:1:1·295:3·18	7·33	3	)·03	118·7 / 86·1	149·8 / 69·3	178·5 / 65·9	209 / 67·9		6·4 / 4·7	29·8 / 13·9	75 / 27·7	103·3 / 33·4	152·6 / 47·5	209
No. 200 0·6:1:2·2:4·72	0	0	0	77 / 100	131 / 100	164 / 100	194·3 / 100	228·7 / 100						
No. 200 0·55:1:2·2:4·72					143·6 / 109·1	170 / 103·7	200 / 103	249 / 108·8						
No. 200 0·65:1:2·2:4·72					104·7 / 79·4	146 / 89	193·3 / 99·5	195·7 / 85·4						
No. 200 0·7:1:2·2:4·72					87·3 / 66·7	115·8 / 70·2	139 / 71·6	205 / 89·6						
No. 200 0·55:1:2·2:4·72	7·23	3	0·03		172·3 / 131·2	185·5 / 113	204·3 / 105·3	272·6 / 118·2		68·3 / 52·1	114 / 69·5	146 / 75·2	184·7 / 80·6	
No. 200 0·65:1:2·2:4·72	8·66	3	0·03		150·7 / 115	174·1 / 166·1	187·3 / 96·3	248·7 / 108·7		36·3 / 27·7	66·6 / 40·6	115·7 / 59·6		190
No. 200 0·7:1:2·2:4·72	9·33	3	0·03		136 / 103·9	136·5 / 83	155 / 79·9	249·6 / 95·9		38 / 29	72·6 / 44·3	101·7 / 52·1	134·6 / 58·7	197

%additive = % by weight of additive in cement; Tri = Triethanolamine; dy = days; mos = months

Table 17. Effects of Differing Water-Ash Ratios on the Strength of Cold Concrete

Table 8. $NaNO_2$ Dose Selection Tests

Additive		Maint. temp. (°C)	Str. Char.	Compression strength (kg/cm^2)					
				3 days	7 days	14 days	28 days	2 mos	3 mos
$NaNO_2$	3 % +		Fr str	47·5	80·5	90	98·7	126	94
Na_2SO_4	3 % +	—10	St str	5·3	19	30	42	56	62
$N(C_2H_4OH)_3$	0·05		Comp vl	9	4·3	3	2·4	2.3	1·5
$NaNO_2$	5 % +		Fr str	36·5	63·1	87·5	122	117	121
Na_2SO_4	3 % +	—10	St str	5·3	23·8	41·1	67·3	81·3	82
$N(C_2H_4OH)_3$	0·05		Comp vl	7	2·7	2·1	1·8	1·4	1·5
$NaNO_2$	6 % +		Fr str	38·7	74	114	129	117	141
Na_2SO_4	3 % +	—10	St str	8·4	34·2	85	67	76	90
$N(C_2H_4OH)_3$	0·05		Comp vl	4·6	2·2	1·3	1·9	2·0	1·6
$NaNO_2$	7 % +		Fr str	28	52	83	107	113	113
Na_2SO_4	3 % +	—10	St str	4·2	24	49	80	93	107
$N(C_2H_4OH)_3$	0·05		Comp vl	6·7	2·2	1·7	1·3	1·2	1·1
$NaNO_2$	8 % +		Fr str	29	36	73	98	107	110
Na_2SO_4	3 % +	—10	St str	2·9	19	48	76	102	114
$N(C_2H_4OH)_3$	0·05		Comp vl	9·8	1·9	1·5	1·3	1	1

Maint. temp. = Maintenance temperature
Str. char. = Strength characteristics
Fr str = Frozen strength
St str = Structural strength
Comp vl = Comparative value

mos = months

Table 18. Relationship Between Frozen Strength and Structural Strength

The tests indicated the following points.

1. The early-phase frozen strength of the cold concrete was greater than its structural strength. As maintenance time was prolonged, structural strength gradually approached zero and the comparative value for frozen strength and structural strength gradually approached 1.

2. When the maintenance temperature was lower than the originally designed freezing point during the process of the hardening of the cold concrete, ice formed within the interior of the concrete and the ice content at that time was closely related to the $NaNO_2$ content and the frozen strength. When the $NaNO_2$ content was low and the ice content was high, frozen strength was high. When the $NaNO_2$ content was high and the ice content was low, frozen strength was low. When the amounts of $NaNO_2$ added were 6% or less, there were comparatively bigh comparatively high frozen strengths up to the 7th day, whereas frozen strengths were greater than structural strengths throughout the entire period after the 14th day. The fact that the comparative values for cold periods of 3 months were over 1.5 indicates that the difference between the designed freezing point and the maintenance temperature was comparatively great, that the concrete was subjected to freezing to differing degrees and that the structural strengths at these times cannot be utilized. When the amounts of $NaNO_2$ added were 7 to 8%, there were, similarly, comparatively high frozen strengths up to the 7th day. However, after the 14th day, the comparative values decreased to a comparatively great extent, while structural strengths increased comparatively rapidly. After cold periods of 2 months, the comparative values were basically similar, indicating that the designed freezing points and the maintenance temperatures were in basic conformance with each other. Although small amounts of ice were present within the concrete, the concrete did not suffer any damage from freezing. Therefore, there was a continuous growth in structural strength and early-phase strength could be utilized.

3. When the freezing point and the maintenance temperature were in conformance with each other under maintenance conditions of -10° C and when loss of strength in the late phase is guaranteed to be less than 10% (see numerical data of Items 2 and 8 in Table 14), early phase frozen strength can be utilized.

5. <u>Strength of Cold Concrete in Resisting Damage by Freezing</u>

During winter when construction is being carried out under extreme cold, natural air temperature is usually between -20 and -30° C. At -10° C, poured cold concrete is not subject to damage by freezing when a long time is required for premaintenance. This is a major parameter in cold concrete construction technology. For this reason, we conducted tests on strength in resisting damage by freezing. In the tests, we used No. 200 cold concrete samples with water-ash ratios of 0·55 and 0·65. After artificial mixing and shake formation were carried out under normal temperature conditions, the samples were ommediately placed in a freezing compartment where they were kept for periods of 3, 5, 7 and 9 days at -10° C. Determinations were made of compression strength in each case, after which the test samples that had been subjected to the aforementioned cold periods were placed separately in freezing compartments at -20° C and kept at that temperature for 2 days. Determinations were made of their compression strengths, after which they were once again in a freezing compartment at -10° C and kept at that temperature for periods of 25, 23, 21 and 19 days. Determinations were made of cold 28-day strength. The remaining test samples were transferred to positive temperatures and subjected to standard maintenance for 28 days. Determinations were made of normal 28-day strength, i.e., 2-month strength, and their strength was compared with that of the 28-day strength, i.e., 2-month strength, of samples kept at -10° C. Table 19 and Figure 3 show the test results.

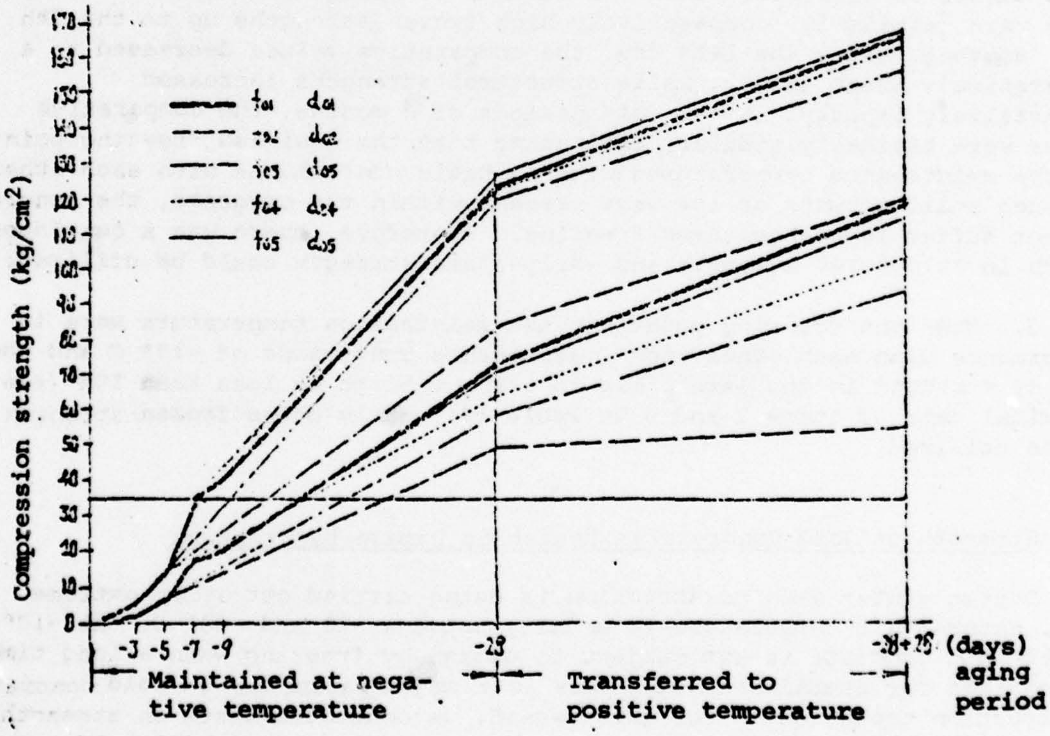

Figure 3. Strength of Cold Concrete in Resisting Damage by Freezing

Serial numbers	Marker number / compounding ratio	Maintained at - 10° C		a)		b)		Loss of strength (%)	
		days	Strength (kg/cm2)	-28 (days)	-28 +28 (days)	-28 (days)	-28 +28 (days)	-28 (days)	-28 +28 (days)
f01		28	123	123	165	100	100	—	—
f02		3	7	81	119	68	72	32	28
f03	200* / 0·55:1:2·2:4·72	5	14·5	119	156	96·5	94·5	3·5	5·5
f04		7	35	122	163	100	99	—	1·0
f05		9	41	126	166	102	100	—	—
d01		28	74	74	118	100	100	—	—
d02		3	3	50	55	67·5	47	32·5	53
d03	200* / 0·65:1:2·2:4·72	5	6·4	59	93	80	78·5	20	21·5
d04		7	18·5	61	103	86·5	87	13·5	13
d05		9	21	71	114	96	97	4	3

Table 19. Loss of Strength of Cold Concrete After Freezing

a) $\frac{\text{Compression strength (kg/cm}^2\text{)}}{\text{Sum of number of days kept at -10° C before and after freezing}}$

b) $\frac{\text{Strength of frozen test samples}}{\text{Strength when maintained at -10° C}}$ (%)

The tests indicate the following points. Loss of strength decreased as the period of early-phase maintenance was prolonged. There was almost no loss in the strength of cold concrete with a water-ash ratio of 0.55 when it was kept at -10° C for 7 days, frozen for 3 days at -20° C and then maintained at -10° C for 21 days or in the strength of concrete transferred to positive temperature conditions for 28 days. These findings were basically similar to those for the strength of concrete maintained at -10° C. This indicates that cold concrete maintained at -10° C for 7 days acquuires a strength of 35 kg/cm^2) i.e., that it can withstand a low temperature of -20° C. Cold concrete with a water-ash content of 0.65 that was maintained at -10° C for 14 days could withstand a low temperature of -20° C without undergoing damage. From the curve in Figure 3, it can be seen that the critical strength at this time was 35 kg/cm^2.

Figure 4 and Figure 5 show the test curves for the strengths of No. 200 and No. 400 cold concrete in resisting damage by freezing. The abscissa in the figures indicates the time when the cold concrete was transferred from negative temperatures (aging period of 3 months) to positive temperature. From the curves, it can be seen that strength continued to increase when the cold concrete was transferred from -20° C to -10° C and that strength increased rapidly to design strength when it was then transferred to and maintained at positive temperature. From a comparison of both curves, it can be seen that the premaintenance time for high marker number concrete was shorter. If a strength of 35 kg/cm^2 is used as an index of judgment, damage by feezing to No. 400 concrete can be prevented by maintaining it -10° C for 3 days, whereas a period of 5 days is required for No. 200 concrete.

From this it can be ascertained that the premaintenance period at -10° C for cold concrete should be controlled on the basis of the critical strength and that it is directly related to the marker number of the concrete, the water-ash ratio and the negative temperature of early-phase maintenance.

The representative characteristics of concrete after early-phase freezing are as follows. The strength of the concrete is very low and its strength when it is once again subjected to maintenance at normal temperature cannot reach the design marker numner. When the degree of freezing differs, loss of strength also differs. If the concrete is frozen immediately after pouring, loss of strength is about 50%. If it is maintained at normal temperature for less than 12 hours before freezing, then loss of strength is about 16%. If it is maintained at normal temperature for more than 24 hours before freezing, then there is basically no loss of strength. The strength of the bond between the concrete and the steel bars is weakened. The capacity of the concrete for resisting infiltration may be deficient. The capacity of the concrete to resist freezing is decreased. For these reasons, concrete poured during winter should under no circumstances be subjected to freezing.

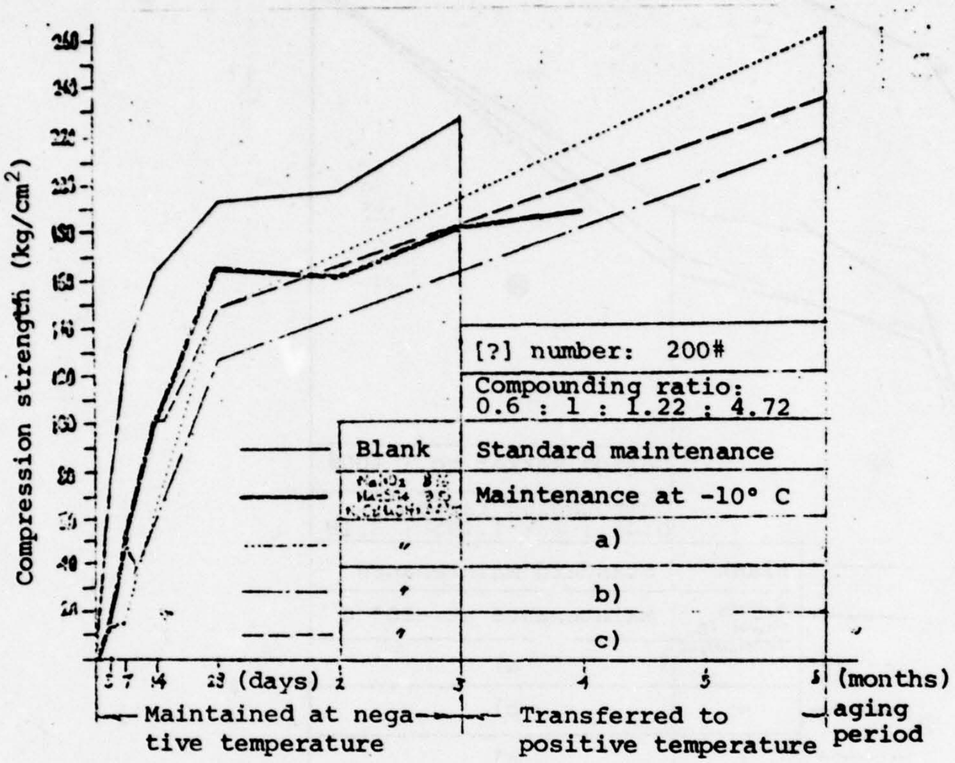

Figure 1. Strength of 200# Cold Concrete in Resisting Damage by Freezing

a) Maintained at -10° C for 3 days and at -20° C for 3 days; maintained at -10° C for 23 days, then maintained at positive temperature for 3 months

b) Maintained at -10° C for 7 days and at -20° C for 3 days; maintained at -10° C for 21 days, then maintained at positive temperature for 3 months

c) Maintained at -10° C for 14 days and at -20° C for 3 days; maintained at -10° C for 14 days, then maintained at positive temperature for 3 months

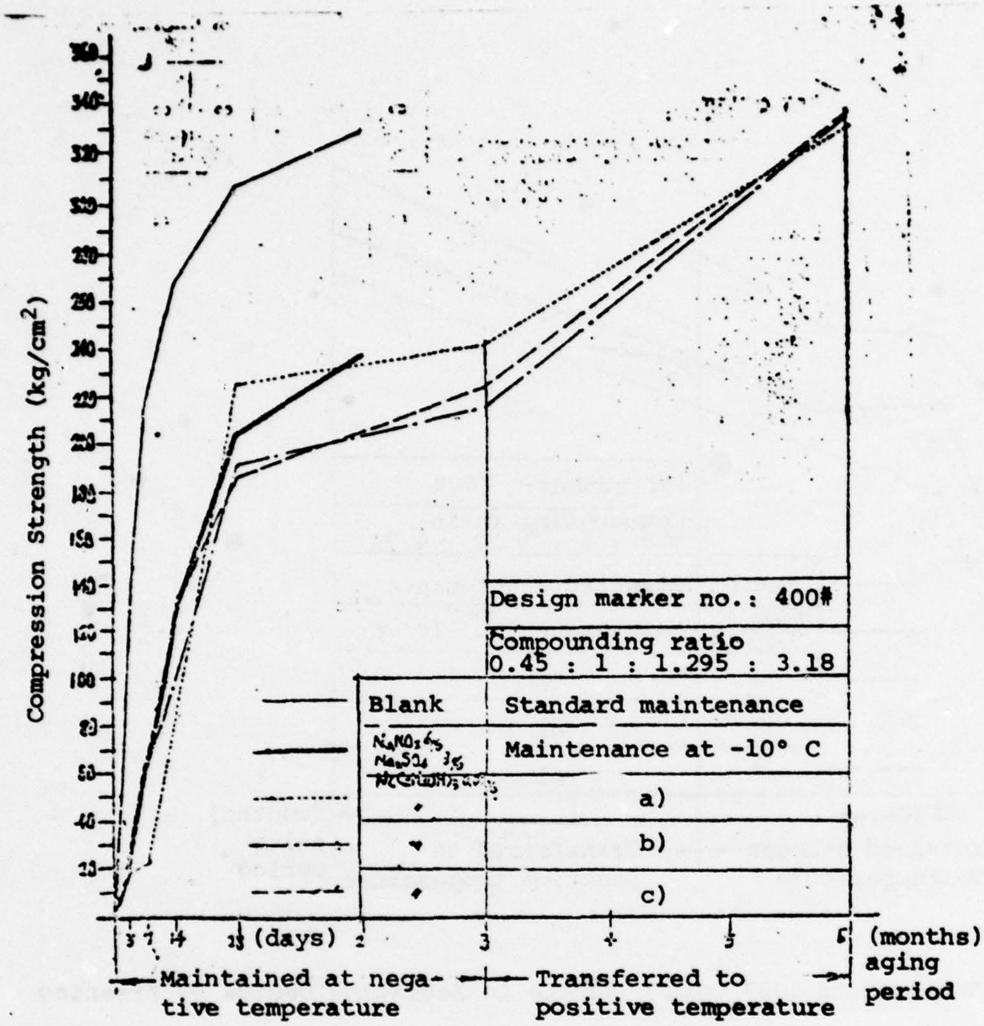

Figure 5. Strength of 400# Cold Concrete in Resisting Damage by Freezing

a) Maintained at -10° C for 3 days and at -20° C for 3 days; maintained at -10° C for 23 days, then maintained at positive temperature for 3 months

b) Maintained at -10° C for 7 days and at -20° C for 3 days; maintained at -10° C for 21 days, then maintained at positive temperature for 3 months

c) Maintained at -10° C for 14 days and at -20° C for 3 days; maintained at -10° C for 14 days, then maintained at positive temperature for 3 months

The following methods were used for the purpose of discriminating early-stage freezing of concrete:

1. An iron hammer is used to strike the structure. If the sound is muted and if an empty sound occurs, this indicates that the structure is brittle and loose. If concrete that is not frozen is struck with a stone, the sound is clear and crisp, indicating that the structure is dense.

2. An iron hammer is used to strike the angles of the structure. If large pieces fall off, the concrete mixture is brittle and loose and the skeletal material is of poor adhesiveness. If large portions of the skeletal material and the concrete mixture become separated from each other, the vertical matter can be pulverized with the hands. Concrete that has not frozen is hard and the concrete mixture and the skeletal material are closely bound to each other. When it is struck, the skeletal material can be pulverized.

3. When pieces of concrete that have been knocked off are examined, water-line traces can be found at the points where the concrete mixture and the skeletal material were joined. This is because a type of ice film is formed on the surface of the skeletal material when concrete is poured during winter, the traces being left after the ice has melted. This phenomenon does not occur in concrete that has not been frozen. This is a major indicator of whether or not freezing has occurred.

4. When the strength of the structure is measured with a resiolometer, a very low resilience value indicates very low strength.

5. Concrete that has been frozen has a dark color that gives a person a melancholy feeling. Concrete that has not been frozen has a deep gray color.

6. Properties of Cold Concrete

In order to facilitate the application and wider use of cold concrete, we made initial determinations of its mechanical properties and its durability. The concrete was subjected to artificial mixing and shake formation under positive temperature conditions, after which some of it was placed in a freezing chamber at -10° C and maintained there for 3 months. Following that, it was transferred to positive temperature and subjected to standard maintenance for 1 month. The other portion was used in comparative tests in which it was subjected to standard maintenance for 4 months in a standard maintenance environment together with ordinary concrete test samples.

Among the mechanical tests, we used cubic test samples of 10 x 10 x 10 cm for determining compression strength, with compression strength of the 10 x 10 x 10 cm test samples being determined by the side splitting method. The modulus of compression elasticity was found for 10 x 10 x 30 cm test samples using a Martens mirror type expansion meter to determine deformation values of 0.4 grade axial compression strength. The bond strength of the steel bars was determined by extraction of ϕ 16 circular steel embedded in 10 x 10 x 20 cm cuboid samples. Tests of resistance to infiltration were conducted with ϕ 15 x 15 cm cylinders using an osmometer.

Among the durability tests, the resistance to freezing tests were conducted by the slow alternation test method in which 10 x 10 x 10 cm test samples were air-frozen in a freezing chamber at -20° C for 4 hours and then melted for 4 hours in water at +15° C, with determinations being made of loss of strength and change in external appearance for differing numbers of freezing and melting cycles. Carbonization and alternating dry-wet tests were conducted using 4 x 4 x 16 test samples made of a cement-concrete mixture. After artificial mixing and shake formation, some of the test sample was placed in a freezing chamber at -10° C for 6 months, while another portion together with a blank concrete mixture test sample were kept under conditions of standard maintenance for 6 months, after which comparisons were made. The carbonization tests were carried out in sealed condainers having a CO_2 concentration of about 70%, with carbonization strengths and carbonization coefficients being determined for various periods of cold. In the alternating dry-wet tests, the test samples were dried at 100° C for 4 hours and then immersed in water and saturated for 4 hours, a procedure that was repeated 30 times. Determinations were made of strength and softening coefficients. The results of the tests are shown in Table 20, 21 and 22.

The following points could be ascertained from the tests.

1. Except for the fact that findings for the modulus of elasticity and resistance to infiltration tended to be low, the indices for the mechanical properties of cold concrete were close to those for ordinary concrete.

2. Cold concrete that was maintained in a positive temperature environment had comparatively good mechanical properties. This was because of great increases in structural density, bond strength of the steel bars and resistance to infiltration. Its superior resistance to infiltration has opened up new possibilities for breakwater concrete.

3. Cold concrete exhibited good resistance to freezing and good durability.

4. The carbonization tests indicated that the carbonization coefficient of cold concrete tends to increase gradually as the carbonization cold period is prolonged.

5. Alternating dryness and dampness did not have deleterious effects on cold concrete.

Water ash ratio	% by weight of additive in cement			Hardening conditions	Mechanical index (kg/cm^2)					
	$NaNO_2$	Na_2SO_4	$N(C_2H_4OH)_3$		Compr str	Axial com st	Tors resist	St bar bd str	Mod compr elasticity	Resist to infiltr
0·6	0	0	0	Stand maint +15°C 4 months	226	250	16	28	$23 \cdot 5 \times 10^4$	
0·6	8	3	0·03	Same as above	260	223	17	38	$22 \cdot 7 \times 10^4$	greater than 20
0·6	8	3	0·03	Stand maint -10°C 3 mos; st mt 1 mo	197	169	17	45	16×10^4	4
0·45	0	0	0	Stand maint +15°C 4 months	313	300	17	29	$21 \cdot 5 \times 10^4$	6
0·45	6	3	0·03	Same as above	316	350	21	50	$23 \cdot 4 \times 10^4$	greater than 27
0·45	6	3	0·03	Stand maint -10°C 3 mos; st mt 1 mo	244	204	19	43	$16 \cdot 9 \times 10^4$	5

Table 20. Mechanical Properties of Cold Concrete

Stand maint = Standard maintenance
St mt = Standard maintenance
mo = Month
mos = Months

Compr str = Compression strength
Axial com st = Axial compression strength
Tors resist = Torsional resistance
St bar bd str = Steel bar bond strength
Mod compr elasticity = Modulus of compression elasticity
Resist to infiltr = Resistance to infiltration

			0·6	0·6	0·6	0·45	0·45	0·45
Water-ash ratio			0·6	0·6	0·6	0·45	0·45	0·45
% by weight of additive in cement	$NaNO_2$		0	8	8	0	6	6
	Na_2SO_4		0	3	3	0	3	3
	$N(C_2H_4OH)_3$		0	0·03	0·03	0	0·03	0·03
Hardening conditions			+15°C st mnt 4 mos	+15°C at mnt 4 mos	-10°C 3 mos, st mnt 1 mo	+15°C st mnt 4 mos	+15°C st mnt 4 mos	-10°C 3 mos, st mnt 1 mo
Compression strength (kg/cm^2) when the number of alternating cylces was	50th time	Test strength	197	265	223	286	346	279
		Freeze-melt strength	197	258	194	313	312	221
		Change in strength	0	—3%	—13%	+9%	—10%	—20%
		External appearance	no change	no change	sm strip on side	no change	no change	no change
	100th time	Test strength	214	253	235	361	362	296
		Freeze-melt strength	205	240	234	337	353	248
		Change in strength	—4%	—5%	0	—8%	—2%	—17%
		External appearance	no change	no change	str sm pl on surf	no change	no change	no change
	150th time	Test strength	197	253	188	286	253	237
		Freeze-melt strength	185	232	181	258	326	278
		Change in strength	—7%	—8%	—4%	—10%	+29%	+7%
		External appearance	strip at top	vy slt cracks	vy slt cracks	cracks	good	good
	200th time	Test strength	197	253	188	286	253	237
		Freeze-melt strength	162	251	191	276	342	281
		Change in strength	—13%	0	+1%	—4%	+36%	+19%
		External appearance						

Table 21. Freezing Resistance Properties of Cold Concrete
(Key on following page)

Key to Table 21:

st mnt	=	standard maintenance
mo	=	month
mos	=	months
sm strip	=	some stripping
str sm pl on surf	=	stripping at some places on surface
vy slt	=	very slight

% by weight of additive in cement $NaNO_2$ Na_2SO_4 $N(C_2H_4OH)_3$	Hardening conditions	Strength after dry-wet alt 30 t			Carbonization strength (kg/cm^2)								
					7 days			28 days			3 months		
		a)	d)	e)	a)	b)	c)	a)	b)	c)	a)	b)	c)
Blank sample	stand mnt 6 months	179	197	1·1	314	303	0·96	287	338	1·17	325	470	1·46
6+3+0·05	"	132	149	0·82				289	227	0·78			
6+3+0·05	-10° C, 6 months	99	136	1·38	188	203	1·08	164	201	1·22	189	296	1·57

Note: The water-ash ratio of the concrete mixture was 0.55.

Table 22. Tests of Alternate Drying and Wetting of Cold Concrete Mixtures and Carbonization Tests

cem. = cement
stand mnt = standard maintenance
strength after dry-wet alt 30 t = Strength after alternate drying and wetting 30 times

a) Test check strength
b) Carbonization strength
c) Carbonization coefficient
d) Alternate dry-wet strength
e) Softening coefficient

7. The Problem of Rusting and Corrosion of Steel Bars in Cold Concrete

(1) The rust-preventing action of $NaNO_2$

$NaNO_2$ in the concrete medium (pH = 10-13) serves as an anodic rust-preventing agent. It prevents rusting by reducing the anode area that is readily subject to rusting and corrosion. When an insufficient quantity is added or when the pH of the medium is changed, anodic processes will still be inhibited, but, at the same time, activation of cathodic processes will be stimulated, with the result that local rusting and corrosion will be induced. This type of rusting and corrosion is much more dangerous than homogeneous rusting and corrosion. Therefore, when $NaNO_2$ is used as a rust-preventing agent, the critical concentrations in different media must be carefully determined in order to avoid inducing cathodic activation and the consequent local rusting and corrosion due to addition of insufficient quantities or unnecessary waste due to addition of excess amounts.

The electrochemical quick method and the quick alternate drying and wetting method were used in the tests and the test specimens were compared.

1. Electrochemical quick method

In these tests we used a 1 : 3 cement-concrete mixture and a water-ash ratio of 0·55. The cement used was No. 500 silicate cement produced in Harbin. For the steel bars, we used No. 3 machining steel of specification ¢ 6 and of a length of 120 mm. The dimensions of the test samples were 4 x 8 x 16 cm. After the test samples were formed and molded, they were kept in steam for 14 hours, after which they were kept indoors and maintained under natural conditions for 40 days. At the time of determination, the steel bars were subjected to polarization at differing current density levels. After a stable state had been maintained for 10 minutes, the polarization potentials corresponding to each current density level were determined. The results are shown in Table 23 and Figure 6.

The following points should be evident from Table 23 and the polarization curves in Figure 6.

(1) In blank test samples containing no additive, the anodic polarization potential shifted very rapidly in the positive direction, deoxidation potential was reached,and the steel bars were in an inactive state so that rusting and corrosion could not be induced.

(2) In test samples containing 2% NaCl, anodic polarization was slow as indicated by the smoothness of the polarization curve, with a state of activation being presented. Thus, it can be seen that NaCl is an agent that accelerates rusting and corrosion so that the presence of NaCl can stimulate the occurrence of rusting and corrosion in concrete.

Additive	Electrode	Polarization potential (mV)				State of steel bar
		V_0	V_5	V_{10}	V_{30}	
Blank sample	anode	—387	+624	+657	+738	Not activated
	cathode	—359	—702	—878	—1250	
NaCl 2%	anode	—657	—537	—417	—80	Activated
	cathode	—600	—785	—928	—1238	
NaCl 2% + $NaNO_2$ 2.2%	anode	—434	+603	+637	+716	Not activated
	cathode	—436	—684	—823	—1170	
NaCl 2% + $NaNO_2$ 4.4%	anode	—356	+614	+651	+721	Not activated
	cathode	—345	—656	—762	—1152	
NaCl 2% + $NaNO_2$ 5.5%	anode	—347	+615	+663	+782	Not activated
	cathode	—362	—661	—730	—1183	
NaCl 2% + $NaNO_2$ 7.2%	anode	—353	+618	+663	+780	Not activated
	cathode	—290	—613	—704	—964	

Note: Average values for test samples of 2 groups were used above.

Additive	Electrode	V_0	V_5	V_{10}	V_{30}	State of steel bar
Na_2SO_4 3%	anode	—415	+580	+620	+713	Not activated
	cathode	—475	—896	—1187	—1316	

Table 23. Na_2SO_4, $NaNO_2$ and NaCl Polarization Potentials

(3) When the amount of NaCl added was 2% by weight of the cement and when differing amounts of $NaNO_2$ were added as a rust-preventing agent, there were marked decreases in the extent of rusting and corrosion of the steel bars as the amount of $NaNO_2$ added was increased. When the $NaNO_2$ content was 4.4% (by weight of the cement), no rusting or corrosion whatsoever of the steel bars occurred. When the $NaNO_2$ content was further increased, the effects were basically similar to those when 4.4% was used.

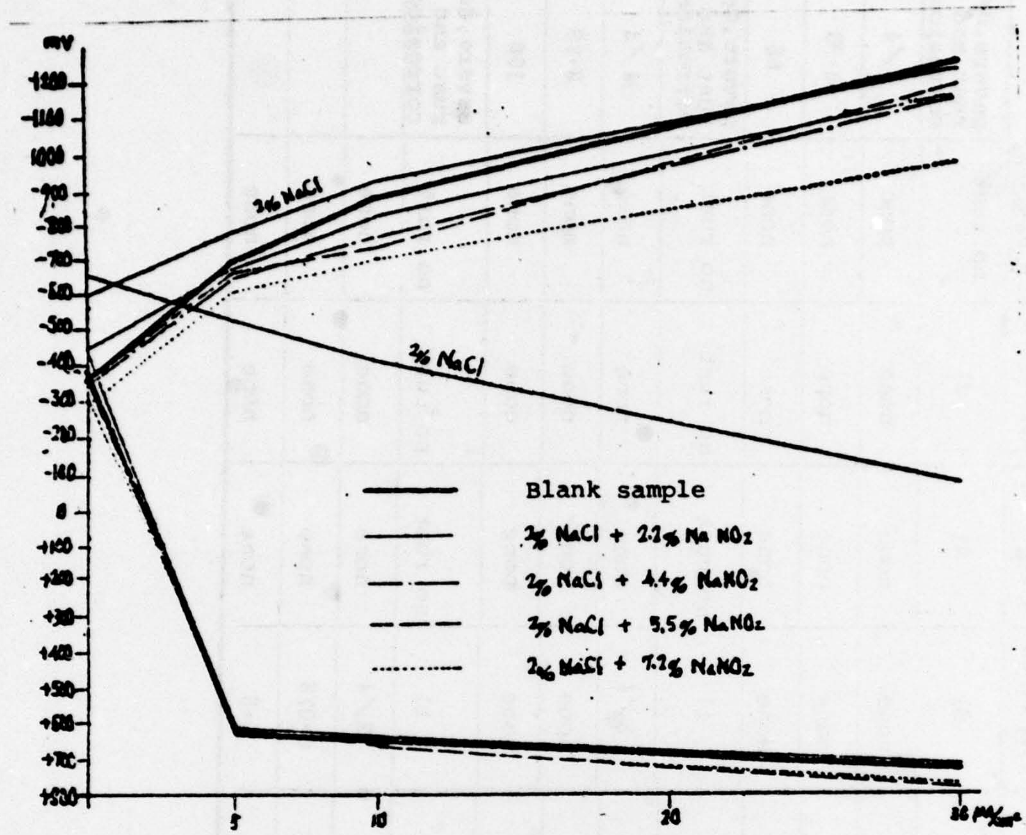

Figure 6. Sodium Nitrite Rust Prevention Polarization Curves

2. Quick alternate drying and wetting method

The test samples were formed in the same way as for the electrochemical method, after which they were subjected to standard maintenance for 7 to 10 days. They were then kept in steam at 100° C for 4 hours, dried at 105-110° C for 3 hours and then set aside indoors for 17 hours. The foregoing procedure constituted one cycle. This procedure was repeated 30 times. After each 10th cycle, one batch of test samples was broken open and direct observations were made of the condition of the steel bars. The results of the tests are shown in Table 24.

Amount of additive		Blank sample	2% NaCl	2% NaCl + 2·2% $NaNO_2$	2% NaCl + 4·4% $NaNO_2$	2% NaCl + 5·5% $NaNO_2$	2% NaCl + 7·2% $NaNO_2$	3% Na_2SO_4 + 8% $NaNO_2$ + 0·03% 三乙	2% $CaCl_2$
10th time	Condition of steel bar	a)	b)	c)	d)	d)	d)	no rust	severe, deep rust and corrosion
	e)	3/4	4/4	4/4	none	none	none	none	4/4
	f)	none	0·78	none	none	none	none	none	0·93
	g)	none	50	none	none	none	none	none	66
20th time	Condition of steel bar	rust spots at ends	severe rust and corrosion	h)	i)	no rust	no rust	no rust	severe, deep rust and corrosion
	e)	4/4	4/4	4/4	2/4	none	none	none	4/4
	f)	0·007	2·1	0·11	none	none	none	none	3·79
	g)	5·2	60	12·1	none	none	none	none	100
30th time	Condition of steel bar	rust spots at ends	j)	k)	l)	no rust	no rust	no rust	severe, deep rust and corrosion
	e)	2/4	4/4	4/4	2/4	none	none	none	
	f)	0·08	6·2	0·23	0·075	none	none	none	
	g)	2·9	99	12·2	1·5	none	none	none	

Table 24. Alternate Drying and Wetting Tests

Key to Table 24:

a) Slight rust and corrosion spots in 1 to 2 places

b) Severe rust and corrosion spots extending over entire strip

c) Slight rust spots in 1 to 2 places

d) No rusting; one-layer of silver-white film on surface of steel bar

e) Number of rusted and corroded bars

f) % by weight of rust and corrosion to total weight

g) % of area of rust and corrosion to total area

h) Rust spots on surface of steel bars

i) Slight punctate rust spots of surface of steel bars

j) Severe and deep rusting and corrosion of the steel bars

k) Severe rust spots on ends

l) Slight rust spots on ends

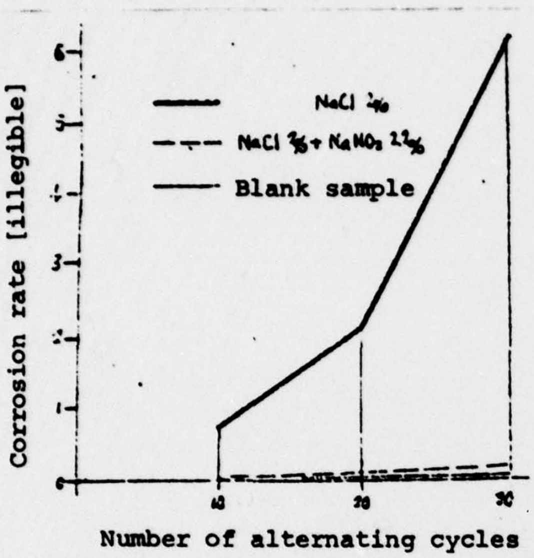

Figure 7. Relationship Between Corrosion Rate and Number of Alternating Cycles [Note: Text of figure is poorly legible.]

The following points can be ascertained from Table 24 and Figure 7.

(1) The steel bars in blank test samples not containing additive had undergone slight rusting and corrosion by the 10th drting and wetting cycle. As the number of cycles increased, rusting and corrosion became more severe, with distinct rust spots appearing on the ends after the 30th cycle.

(2) Distinct rusting and coorosion were found in test samples to which 2% NaCl had been added after the 10th cycle. Moreover, as the number of cycles increased, the area and quantity of rusting and corrosion was markedly increased.

(3) Sodium nitrite had a distinct rust-preventing effect. The addition of 2.2% of $NaNO_2$ to test samples containing 2% of NaCl had an

intense inhibiting effect on the occurrence and expansion of rusting and corrosion of steel bars, with only very slight rust spots being found on the ends after the 10th cycle. Moreover, the increase in the corrosion rate was slowed as the number of cycles increased. As the amount of $NaNO_2$ added was increased, the corrosion rate gradually decreased. When the $NaNO_2$ content was 4.4% by weight of the cement, no rusting or corrosion appeared by the 20th cycle and only very slight rusting and corrsion appeared by the 30th cycle, findings distinctly better than those for the blank test samples. When the $NaNO_2$ content was 5.5% and 7.2%, the results at the 30th cycle were essentially similar to those when content was 4.4%.

From the preceding, the following points can readily be seen. The fact that similar results were obtained by the electrochemical method and the alternate drying and wetting method gives us a much clearer understanding of $NaNO_2$ as a rust preventing agent. While severe rusting and corrosion of steel bars in concrete mixtures or concrete containing 2% of NaCl, occurrence and expansion of rusting and corrosion of steel bars can basically be prevented merely by adding 2.2% of $NaNO_2$ by weight of the cement. When the $NaNO_2$ content reaches 4.4%, there was essentially no occurrence of rusting and coerosion of the steel bars, with the condition of the steel bars being supperior to that of the blank test samples. Further increase of content did not have evident effects.

(2) <u>The effects of 3% Na_2SO_4 on rusting and corrosion of steel bars</u>

Although Na_2SO_4 is used as an additive to accelerate hydration reactions in cement, it may have deleterious effects on the steel bars. For this reason, we conducted tests of sodium sulfate by the electrochemical quick method. The materials and processes used in the tests were the same as indicated previously. The results of the tests are shown in Table 23 and Figure 8. From Table 23 and from the anodic and cathodic polarization curves it can be seen that the addition of 3% of Na_2SO_4 to the cement did not have any deleterious effects on the steel bars, with the steel bars remaining in an inactive state. However, anodic processes were somewhat accelerated as compared to the blank test samples.

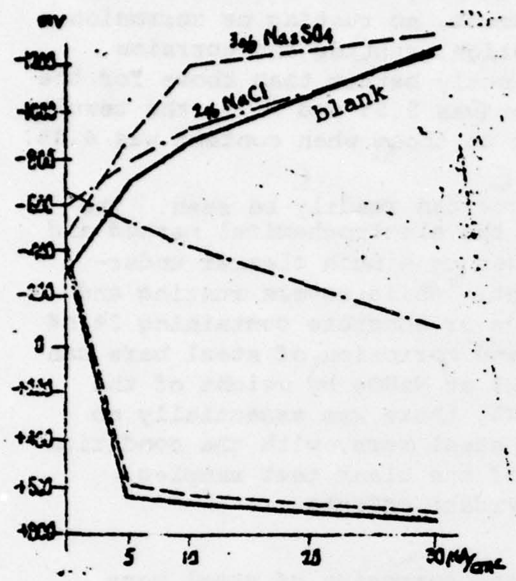

Figure 8. Steel Bar Polarization Curves with 3% Sodium Sulfate

(3) Effects of $NaNO_2$-Na_2SO_4 combined additive on rusting and corrosion of steel bars in concrete

The electrochemical quick method and the quick alternate drying and wetting method were used in the tests. Two types of steel bars were used in the tests, one of which was ordinary A_3 low carbon steel and the other was prestressed low carbon cold drawn steel wire.

1. Table 25 and Figures 9 and 10 show the results of tests using the electrochemical quick method.

As can be seen from Table 25 and Figure 9, the sodium nitrite - sodium sulfate combined additive did not have any deleterious effects on the steel bars in the concrete when ordinary A_3 low carbon steel was used. The results of the electrochemical tests indicated a state of inactivation. When the current density was greater than 10 $\mu A/cm^2$, this type of combined additive caused the polarization potential of the steel bars on the anodic polarization

Additive	a)	Specifications	b)	c)	Polarization potential (mV)				Condition of steel bars
					V_0	V_3	V_{10}	V_{20}	
Na_2SO_4 3% + $NaNO_2$ 8% + $N(C_2H_4OH)_3$ 0·03%	A3	φ6 L=120		e)	—423	+590	+643	+784	Not activated
				e)	—320	—620	—717	—1048	
Same as above	g)	φ5 L=120	d)	e)	—327	+619	+679	+855	Not activated
				f)	—310	—717	—898	—1292	

Table 25. $NaNO_2$ - Na_2SO_4 Combined Additive Polarization Potentials

a) Type of steel bar
b) Surface state
c) Electrode
d) Machined
e) Anode
f) Cathode
g) Cold drawn steel wire

curve to be somewhat higher than the polarization potentials of the blank test samples. This indicates that the extent to which iron atoms on the surface of the steel bar enter the electrolytic solution in the form of iron ions is relatively somewhat less. That is to day, steel bars in concrete containing the combined additive develop rusting and corrosion less readily and are more stable than steel bars in concrete not containing combined additive.

From Table 25 and Figure 10, it can be seen that the sodium nitrite - sodium sulfate combined additive had even better inactivating effects on low carbon cold drawn steel wire,,with the degree of anodic polarization of the steel bars exceeding that of the blank test samples. Therefore, the sodium nitrite - sodium sulfate combined additive not only does not have any harmful effects on cold drawn steel wire but it also has a protective effect on it.

2. The results of the tests using the quick alternate drying and wetting method are shown in Table 24. The test methods and procedures were the same as described previously, As can be seen from Table 24, the $NaNO_2$ - Na_2SO_4 combined additive also functioned as an inactivating agent on the steel bars. after 30 drying-wetting cycles, no rusting or corrosion of the steel bars had occurred, whereas rusting and corrosion had occurred after 30 cycles in steel bars when the chemical additive was not used. Severe and

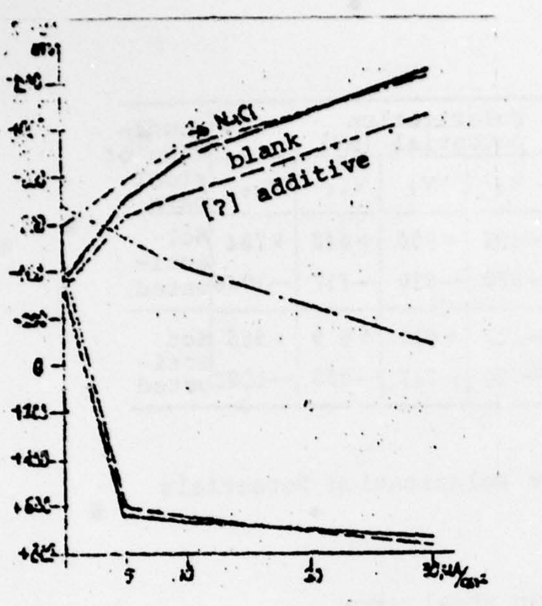

Figure 9. Polarization Curves for Ordinary A_3 Steel Bars

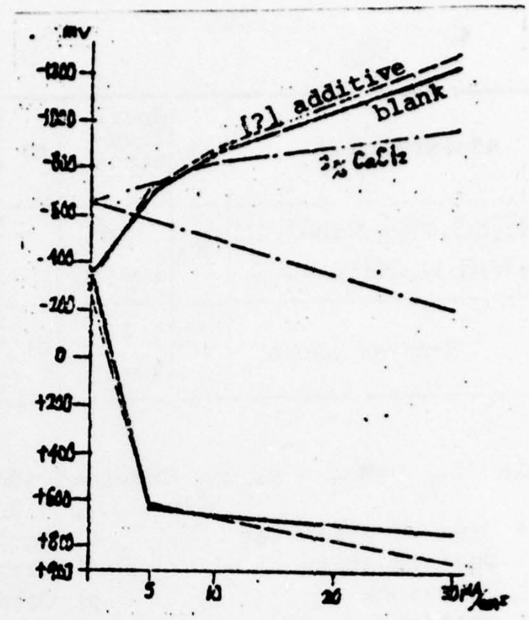

Figure 10. Polarization Curves for Cold Drawn Steel Bars

deep rusting and corrsion occurred after 30 cycles in test samples containing 2% $CaCl_2$ and 2% NaCl.

3. Long-term observation method

Ordinary A_3 low carbon ϕ 8 steel of 6 cm in length was used in the tests. The steel was machined and degreased. Two steel bars were embedded in concrete parallel to and at a distance of 3 cm from each other and with a protective layer of 3 to 4 cm. The dimensions of the test samples were 10 x 10 x 10 cm. The concrete was No. 400 with a compounding ratio of 0.45 : 1 : 1.295 : 3.10. The additive content was 6% $NaNO_2$ + 3% Na_2SO_4 + 0.03% $N(C_2H_4OH)_3$. After the test samples were formed and molded, they were subjected to standard maintenance for 28 days and then transferred to maintenance under natural conditions. The test samples were broken open and observed at various times and comparisons were made with blank test samples.

The results of the tests are shown in Table 26.

% by weight of additive in cement	Maintenance under natural conditions	
	6 months	1 year and 6 months
Blank test samples	No rusting	No rusting
$NaNO_2$ 6% + Na_2SO_4 3% + triethanolamine 0.03%	No rusting	No rusting

Table 26. Tests by the Long-Term Observation Method

In summary, similar results were obtained by means of the three test methods. The $NaNO_2$ - Na_2SO_4 combined additive did not have any deleterious effects on the steel bars and also had a definite protective action on steel bars in concrete.

8. Conclusions

1. $NaNO_2$ is an antifreeze agent for cold concrete. At -10° C, it can prevent freezing of concrete when it is added in amount of 13.3% of the water content. At the same time, $NaNO_2$ has good plasticizing effects and good effects in slowing condensation of cement. Addition of $NaNO_2$ in an amount of 13.3% of the water content can allow a decrease of about 10% in the water content and results in the fluidity of the concrete remaining unchanged for up to 4 hours.

2. Na_2SO_4 is a very good positive temperature early strengthening agent. When it is combined with $NaNO_2$ at -10° C in an amount of 3% by weight of the cement, it still exhibits a distinct action in stimulating hardening. When the concrete is transferred from -10° C to positive temperature, the strength of the concrete continues to increase.

3. When $N(C_2H_4OH)_3$ is used in an amount of 0.03% by weight of the cement and combined with $NaNO_2$ and Na_2SO_4, it can increase the early-phase strength of the concrete by about 5%. When the samples are transferred to positive temperature, the effects are similar as with Na_2SO_4.

4. With an additive composed of $NaNO_2$ in an amount of 13.3% the water content of the concrete, Na_2SO_4 in an amount of 3% the cement content and $N(C_2H_4OH)_3$ in an amount of 0.03% of the cement content, the concrete

does not undergo damage from freezing at -10° C and its strength increases, more slowly in the early stages and more rapidly in the later stages. When it is kept for long periods at negative temperatures, its strength still increases. At 28 days, over 60% of the design strength can be attained. When it is kept at -10° C for 3 months, 80 to over 90% of the design strength can be attained, with loss of strength in the later stages not exceeding 10%.

If this type of additive is used under positive temperature conditions (+10 to +15° C), it results in an early strengthening effect, good concrete density, resistance to infiltration of up to 28-30 kg/cm^2, strength in the later stages 5 to 10% greater than that of ordinary concrete and physical properties superior to those of ordinary concrete.

5. The water-ash ratio has extremely great effects on cold concrete, with an increase or decrease in the water-ash ratio of 0.05 resulting in an increase or decrease in strength of 30 to 40%. Therefore, when cold concrete is being used, the water-ash ratio must be rigidly controlled, with as low as possible a water-ash ratio being used to allow fluidity for construction.

6. When this type of concrete is maintained at -10° C for 7 to 9 days, it is possible for it to acquire strength in resisting freezing at even lower temperatures. The critical strength value at this time is 35 kg/cm^2. The strength in resisting damage by freezing that is acquired at -10° C is related to the premaintenance period, the water-ash ratio and the cement content but is not related to freezing time.

7. Because of the rust-preventing action of $NaNO_2$, the cold concrete additives do not have any rusting or corroding effects on the steel bars.

8. Except for decreases in the modulus of elasticity and in resistance to infiltration, the physical and mechanical properties of cold concrete do not differ from those of ordinary concrete.

9. The early-phase strength of cold concrete increases slowly. However, compreshensive measures such as hot mixing, regenerative heat maintenance or passing through of small amounts of steam can be taken to raise early strength and enlarge the ranges of its use.

10. The facts that cold concrete is convenient to work with, that the additives can be obtained easily and that the costs are comparatively low make this a method that is well worth adopting and using widely in carrying out construction during winter.

11. There is a problem in respect to the construction specifications for the additive Na_2SO_4 (GBJ10-65) in which it is specified that the sulfate content of the mixing water should not exceed 1% as calculated on the basis of the SO_4. In our long-term observations of test samples with a high content

of 3%, we did not find any damage to concrete except in cases in which the skeletal material exhibits alkaline activity. Many units have conducted research on this topic. The Nanjing Chemical Engineering College has found that the addition of Na_2SO_4 to water increases its alkalinity. For this reason, the use of alkaline skeletal materials of mineral skeletal materials with similar activity can certainly increase the severity of damage involving swelling of the skeletal materials. We must await much further testing and research in order to achieve a fuller understanding of this problem.

There are a number of other problems associated with cold concrete that must be solved by further research and practice in the future. These problems include the range of its uses, the separating out of salts, the technical parameters in smooth mold construction, the adaptability of combined additives to various types of cement, the electric conductivity of cold concrete, resistance to corrosion and the mechanism of hardening.

9. Addendum: Essential Points Concerning Cold Concrete Construction (Discussion Draft)

(1) General principles

1. Definitions and explanations

Cold concrete is prepared using a 13.3% $NaNO_2$ solution in respect to the water content of the concrete and has a specific gravity of 1.08. A concrete additive consisting of 3% Na_2SO_4 and 0.03% $N(C_2H_4OH)_3$ in respect to the water content of the cement can be used in concrete for winter construction and in reinforced concrete construction. At -10° C, 28-day strength reaches about 50% of design strength. When it is transferred to positive temperatures (+10 to +15° C) after 3 months and maintained at such temperatures for 1 month, it reaches over 90% of the design strength. In construction under conditions of severe cold (-20 to -30° C), comprehensive measures must be taken to maintain warmth to assure that the temperature of the concrete itself does not fall below -10° C. Premaintenance for 7 to 9 days can prevent damage by freezing.

2. Materials

(1) Cement: Ordinary silicate cement with a cement marker number not lower than No. 400 should be used.

(2) Course skeletal material: Should satisfy the requirements of GBJ10-65 (revised version) and should not contain frozen matter or ice needles.

(3) The $NaNO_2$, Na_2SO_4 and $N(C_2H_4OH)_3$ should meet standard specifications.

(2) Design of concrete compounding ratios and preparation of solutions

(1) The concrete marker number should not be lower than No. 200, the cement content of each cubic meter of concrete should not be lower than 250 kg, the water-asj eatio should be controlled to within 0.6 and the degree of collapse should be less than 3 cm.

(2) Table 27 shows the $NaNO_2$ content appropriate for various differing air temperatures.

Minimum air temperature when concrete is poured	-3° C	-5° C	-8° C	-10° C
Per water content (%)	3.3	6.6	10	13
Per cement content (%)	2	4	6	8

Table 27. Reference Table for $NaNO_2$ Content

(3) The $NaNO_2$ and the triethanolamine should be prepared in advance as solutions for use. Anydrous sodium sulfate with the appearance of powdery crystals should be used. It can be passed through a sieve to remove large particles and then it can be introduced in the specified quantity directly into the mixer and be mixed with the sand and cement. When crystalline sodium sulfate is used, it should be reduced to anhydrous sodium sulfate. It should first be prepared as an aqueous solution on the basis of the required concentration. After the crystalline sodium sulfate has dissolved, the $NaNO_2$ and triethanolamine can then be added. After they have been completely dissolved by stirring, they can be used in mixing the concrete. The solution should be prepared by a specially assigned person and the accuracy of the concentration should be confirmed.

(4) The temperature of the solution of additives should not be lower than 40 to 50° C.

(3) Mixing of the concrete

(1) The quantity of solution introduced when the cement is being mixed should be rigorously controlled.to assure that the degree of collapse of the mixture will be 2 to 3 cm.

(2) The temperature of the mixture when it comes out of the tank should not be lower than +10° C. Otherwise, the temperature of the solution can be raised to 70 to 90° C or the sandstone can be heated.

(4) Pouring and maintenance of the concrete

(1) Before pouring, the ice and snow should first be removed from the molds and the steel bars.

(2) The temperature of the concrete should not fall below -10° C within the 7 to 9 day period following pouring.

(3) When concrete is poured in air temperatures below -10° C, compreshensive measures for maintaining warmth such as hot mixing, regenerative heat maintenance or passage of small amounts of steam in order to assure that the temperature of the concrete will be in the vicinity of -10° C.

(4) In the case of structures requiring resistance to infiltration, the temperature within the two circumferences after the pouring of the concrete should not be less than -2° C.

(5) Testing of the quality of cold concrete

(1) Determine the concentration and temperature of the additive solution.

(2) Determine the temperature of the mixture when it comes out of the tank and its degree of collapse.

(3) After the concrete is poured, its temperature should be determined once every two hours during the first three days and once every four hours after the first three days. The temperature should be determined at an unfavorable point and the thermometer should be left in the determination hole for 3 to 4 minutes.

(4) At the same, determinations should be made of the temperatures of the air in the surroundings of the construction and of the temperature of the medium.

(5) At the same time that the concrete is being poured, formation tests should also be conducted in 4 groups. In one of these groups, early stage strength should be deremined. In the second group, 28-day strength at negative temperature should be determined. In the third group, determination should be made of 28-day strength at positive temperature after 28 days at negative temperature. In the fourth group, the samples should be subjected to standard maintenance for the purpose of comparative tests.