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Fundamental study on the effectiveness of nitrite for polymer-cement mortar

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ABSTRACT

In this study, experimental examinations are performed to clarify the effects of difference of nitrite-concentration and species on polymer-cement mortar. From experimental results, it is found that the contained nitrite in polymer-cement mortar effectively prevents both carbonation and chloride ion penetration into mortar with the increasing use of nitrite in polymer cement mortar. In case of the addition of lithium nitrite into mortar, there is less effect on liquidity of mortar in comparison with calcium nitrite. Therefore, large volume of lithium nitrite can be added into mortar. However, in case of large amount of addition of lithium nitrite, longer setting time of mortar and other issues were found.

Keywords. Polymer-cement, Lithium nitrite, calcium nitrite, chloride ion, neutralization

1. INTRODUCTION

In recent years, from the viewpoints of maintenance and life cycle management, the deteriorated concrete due to damages from chloride, carbonation and so on, has been repaired using various materials and methods. In case of repairing those damaged concrete structures section, recovery method can be applied. With partial section recovery method (one of the repairing construction methods), damaged structures can be restored to their original state after the removal of the deteriorated concrete areas. However, it has been pointed out that section recovery has a risk of re-deterioration when corrosion inhibitor cannot be applied to every inch of reinforcing bars. On the other hand, in recent years, nitrite has been drawing renewed attention for its high protection. While corrosion control has been recognized as an effect of nitrite, it has been reported that the effects of lithium nitrite-added mortar include increased compressive strength, deterioration inhibition, and so on, (A. KITAGAWA, 1989), (T. HORI, 1991) . Therefore, when the polymer cement mortar used in section recovery method is mixed with the nitrite, re-deterioration problem due to the corrosion inhibitor coating defect and the macrocell corrosion are expected to be solved. However, it has not been clarified about how the difference of species and concentration of nitrite in polymer cement influence the effects.

Therefore, in this study, lithium and calcium nitrite are focused upon and the experimental examinations were carried out in order to clarify the effects of the species of nitrite and

Table 1. Mix proportions

Series	W/C (%)	Unit Content				Concentration of nitrite in mixing water (mol/L)		
		Mixing water (kg/m^3)			Polymer cement(kg/m^3)			
		W	lithium-nitrite	Calcium-nitrite		nitrite	nitrite ion	metal element
Li-10	20	245	27	-	1361	0.047	0.041	0.006
Li-25		205	68	-	1367	0.118	0.103	0.015
Li-50		138	138	-	1380	0.236	0.205	0.031
Ca-5		258	-	14	1358	0.011	0.008	0.003
Ca-10		246	-	27	1367	0.023	0.016	0.007
Ca-25		207	-	69	1380	0.057	0.04	0.017
PCM		271	-	-	1355	-	-	-

concentration of nitrite in polymer cement mortar by discussing the results of the carbonation test, salt immersion test, and corrosion test.

2. EXPERIMENTAL PROGRAM

2.1 Polymer-cement mortar materials

The polymer cement is composed of fine aggregate, glass and vinylon fibre. Replacement of each nitrite for mixing water, “Li-10”, “Li-25”, “Li-50” polymer cement mortar was made with replacement ratio of 10%, 25% and 50% with the mixing water by lithium nitrite. Ca-5, Ca-10, Ca-25 polymer cement mortar was made with calcium nitrite replacing mixing water by 5%, 10% and 25%, respectively. These mix proportions are shown in table 1.

2.2 Mixing and curing

Polymer cement mortar (here in after call “PCM”) were prepared with an handheld electric mixer for 6 minutes on the assumption of that in the case of real construction, as shown in following process (1) ～(3).

(1) Water and lithium or calcium nitrite are added in container, (2) 30 seconds spent in addition of polymer cement in mixer, (3) Mixing for 330 second.

A day after casting, specimens were de-moulded and cured in atmosphere under 20^0C and relative humidity of 60% during different setting periods of 1 or 28 days.

2.3 Testing of specimens

Flow-table and strength tests

Flow-table and strength tests were carried out in accordance with JIS R 5201. Strength test was carried out using specimens of 40*40*160mm at the ages of 1 and 28 days while kept setting in atmosphere.

Pore volume distribution test

Pore volume distribution in each of specimen with a setting period of 28day were measured by mercury intrusion technique (pressure 0～200Mpa).

Accelerated carbonation test

In this examination, prism specimens of 40*40*160mm were used. Specimens were exposed to the environment for 91 days with temperature of 20℃, 60% humidity and 5% CO_2 concentration.

Salt immersion test

In this examination, cylindrical specimens of diameter 100mm and length 100mm were used. After 1 or 28 days of curing, the side and bottom were coated by epoxy resin, except top surface for the test. Specimens were immersed in 10% NaCl solution for 91 days, in accordance with JSCE-572-2003 "the method for apparent diffusion coefficient of chloride ion in concrete by submergence in salt water".

3. RESULTS AND DISCUSSION

Figure1 shows the flow value in each type of mixing mortar. The flow value clearly decreased with increment of nitrite content, in spite of nitrite varieties. Focusing attention on difference of nitrite varieties, flow value of calcium nitrite was lower in comparison with lithium nitrite at the same concentration. Lithium nitrite has less effect on liquidity of mortar in comparison with calcium nitrite. However, mortar casting was barely possible when calcium nitrite concentration of 0.057mol/l included. If more concentration is put in, it was difficult for mixing due to the abnormal setting by the reaction of calcium nitrite and silicate in cement. On the other hand, in case of lithium nitrite more than 0.25mol/l concentration, issue of longer setting time of mortar was found. These results have been reported in other research [1].

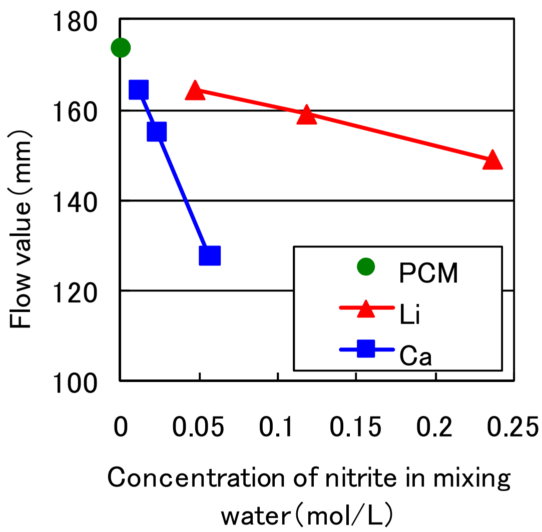


Figure 1. Flow value in each type of mixing mortar

Figure 2, 3 shows the flexural and compressive strength of each types of specimen after 1 and 28 days respectively. In each of nitrite, the flexural and compressive strength were increased with increment of each nitrite contents, and were correlated with the concentration of nitrite. The flexural and compressive strength of lithium nitrite tends to be increased between 1-28 days in comparison with calcium nitrite. Comparing with the difference of metallic element, in case of lithium nitrite, the strength increased in comparison with calcium element at the same concentration. For 28 days, difference of strength was more. From these result, it is found that development of strength was not only influenced by nitrite but also on long term, lithium metallic has an effect on strength development.

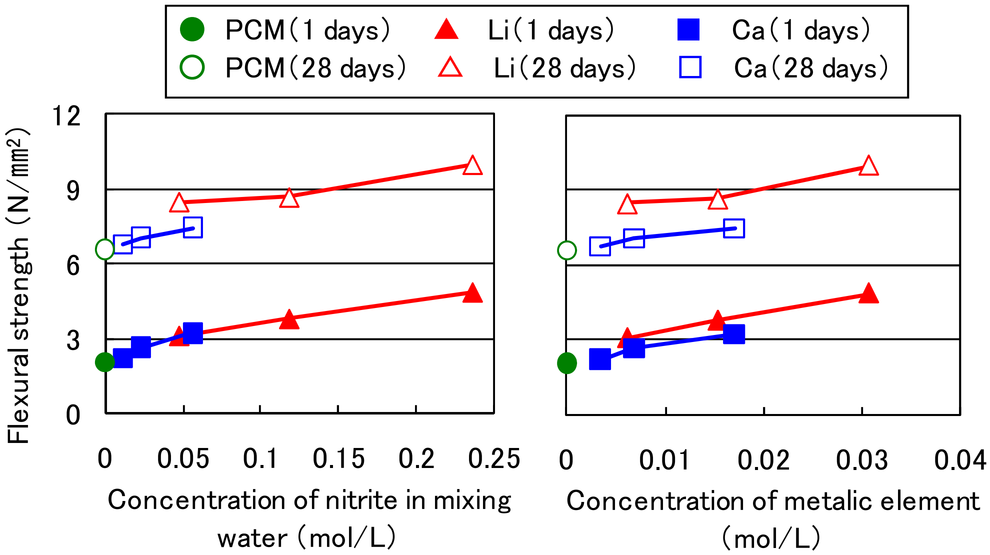


Figure 2. Flexural strength in each type of specimen

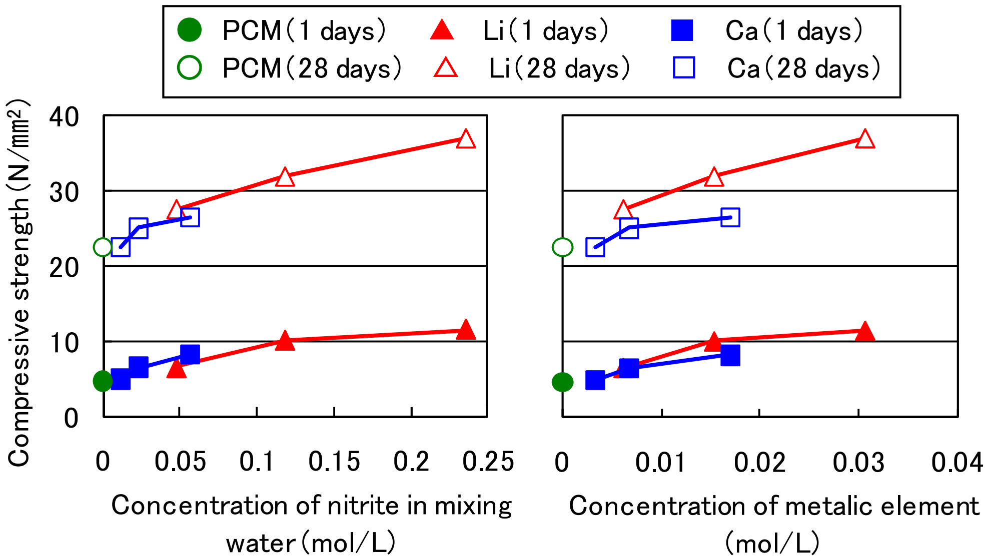
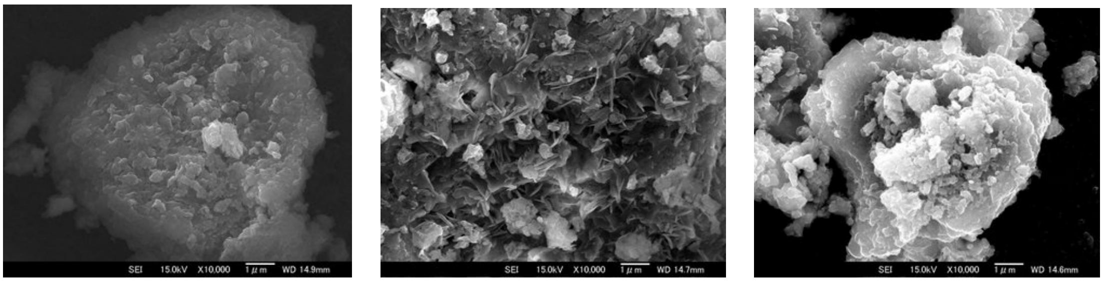


Figure 3. Compressive strength in each type of specimen

Figure 4 shows the structure of crystal in cement paste including any nitrite, measured by scanning electron microscope. From this result, distinction between including calcium nitrite specimen and PCM was not clear, and both crystals were common C-S-H crystal. However, in case of the including lithium nitrite specimen, it was acicular structure that the crystal was distinctly different from crystal of PCM. It was found that lithium nitrite have effect to crystal structure.



(a) PCM (b) Lithium nitrite (c) Calcium nitrite

Figure 4. Structure of crystal in cement paste including any nitrite

Figure 5 shows the total pore volume and capillary pore between 0.015μm to 15μm distribution conditions in the polymer cement mortar with nitrite content after curing for 28 days under the atmosphere. In the range of capillary pores having relatively smaller size, pore volume of calcium nitrite content tend to be less than lithium nitrite, in spite of small amount addition. However, in case of calcium nitrite, it was suggested that pore volume does not correlate with concentration by effect of local reaction with silicate in cement. On the other hand, in case of lithium nitrite, both the total pore volume and capillary pore decreased with the increasing concentration.

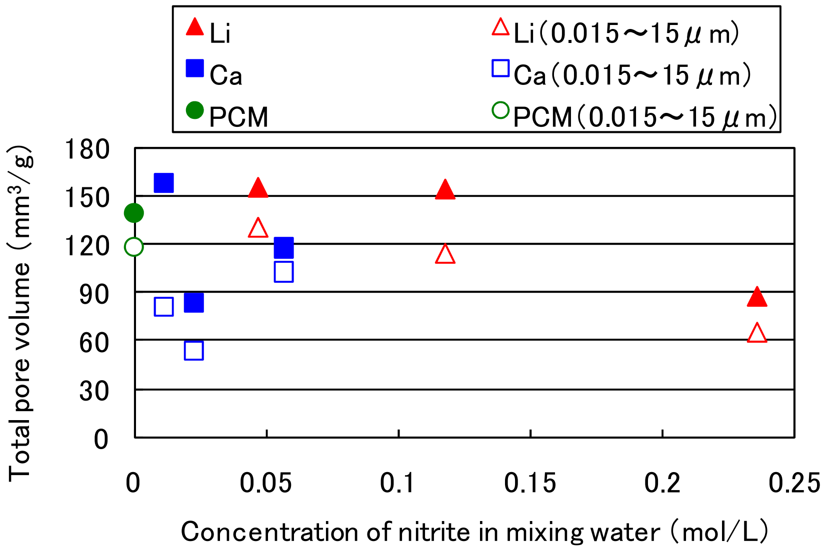


Figure 5. Total pore volume and capillary pore between 0.015μm to 15μm

Figure 6 shows the neutralization depth in each type specimen after 91 days of accelerated neutralization test. The neutralization depth of the specimen clearly decreased with volume of nitrite content, in spite of kind of nitrite and curing period. Comparing with difference of metallic element, the neutralization depth of calcium nitrite content specimen by curing period had no significant difference, and in case of lithium content had a clear difference in the range of low concentration. It means that the lithium can increase the resistance to neutralization in mortar on long term, consistent with strength tests. The lithium specimen had high neutralization resistance in comparison with the calcium specimen; it was suggested that neutralization resistance was affected by crystal structure, water-retentive property of lithium. In addition, it is necessary to consider in detail about other influential factors.

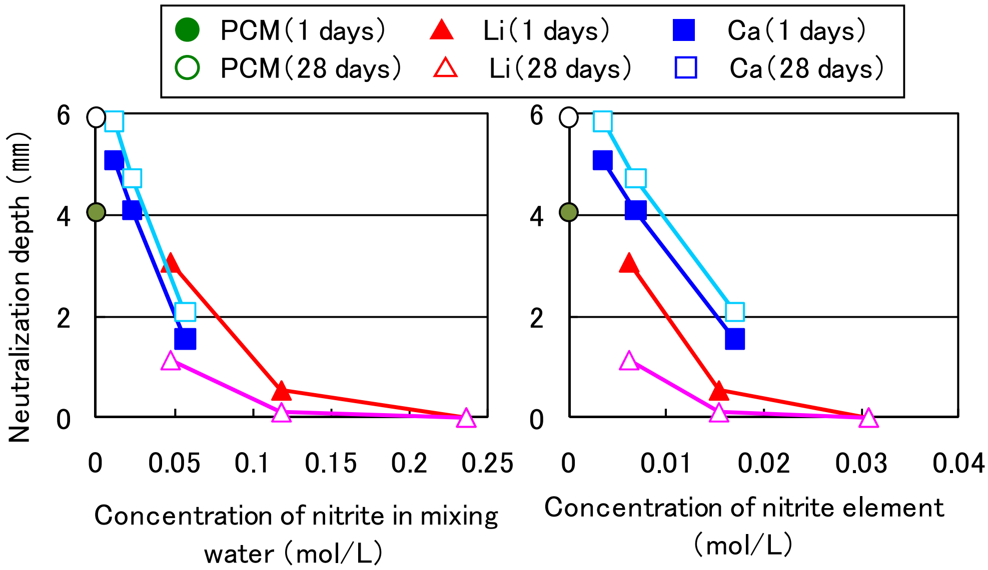


Figure 6. The neutralization depth in each type of specimen after 91 days

Figure 7 shows the result of apparent diffusion coefficient in each type of specimens after 91 days of salt immersion. The apparent diffusion coefficient of all the nitrite content specimens after curing for 28 days was decreased than PCM. Comparing with difference of metallic element, apparent diffusion coefficient has no significant difference between lithium and calcium at curing of 1day. However, in case of the 28 days curing, lithium has decreased in comparison with calcium. Form these result, it was suggest that lithium has some effect on polymer cement mortar.

Figure 8 shows the total capillary pore between 0.015 μ m to 15 μ m distribution conditions with chloride ion apparent diffusion coefficient in each type of specimen. Apparent diffusion coefficient of Calcium nitrite specimens decreased in comparison with PCM, in spite of same total capillary pore. On the other hand, in case of the lithium nitrite specimen, even if the total capillary pore is same with PCM, apparent diffusion coefficient of lithium nitrite specimen decreased comparing to PCM.

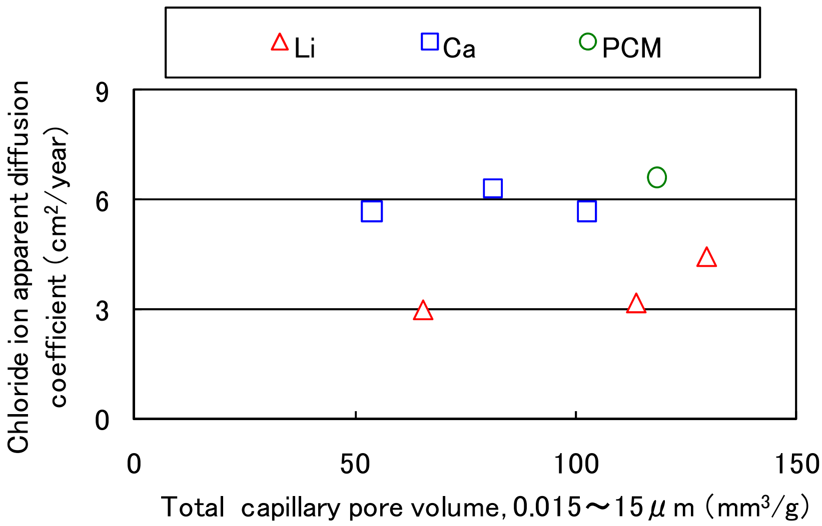


Figure 7. Apparent diffusion coefficient in each type of specimens

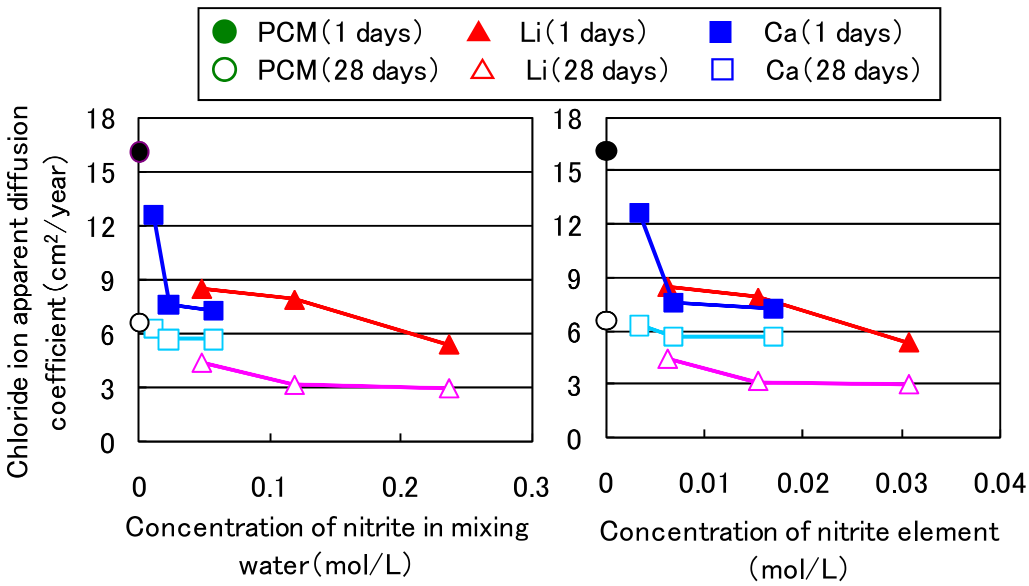


Figure 8. The total capillary pore with apparent diffusion coefficient in each type of specimen

4. CONCLUSION

In this study, focusing on the lithium and calcium nitrite, the experimental examinations were carried out in order to clarify the effects of the species of nitrite and concentration of nitrite in polymer cement mortar by discussing the results of the carbonation test, salt immersion test, and corrosion test, the following conclusions were obtained:

(1) In case of the addition of lithium nitrite in mortar, there is less effect on liquidity of mortar in comparison with calcium nitrite. Therefore, large volume of lithium nitrite can be added into mortar. However, large amount of addition of lithium nitrite results in long setting time of mortar and other issues.

(2) It is found that the contained nitrite in polymer cement mortar can effectively prevent both carbonation and chloride ion penetration into mortar with the increasing use of nitrite.

(3) It is found that development of durability of polymer cement mortar was not only influenced by nitrite but also lithium metallic has no small effect on it.

(4) It is found that development of strength was not only influenced by nitrite but also on long term, lithium metallic has an effect on strength development.

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