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Description	The Thirteenth East Asia-Pacific Conference on Structural Engineering and Construction (EASEC-13), September 11-13, 2013, Sapporo, Japan.
Relation	Proceedings of the Thirteenth East Asia-Pacific Conference on Structural Engineering and Construction (EASEC-13), September 11-13, 2013, Sapporo, Japan, I-2-5.
Citation	Proceedings of the Thirteenth East Asia-Pacific Conference on Structural Engineering and Construction (EASEC-13), I-2-5
Issue Date	2013-09-13
Doc URL	https://hdl.handle.net/2115/54478
Type	conference paper
File Information	easec13-I-2-5.pdf

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FUNDERMENTAL STUDY ON THE PERFORMANCES AND CHARACTERISTICS OF HIGH FUNCTION MORTAR INCLUDING NITRITE

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ABSTRACT

The application of cross section recovery method using nitrite polymer-cement mortar has been examined in the present study. The effects have not yet been quantitatively analyzed. Experimental examinations are performed to clarify the effects of calcium and lithium nitrite in mortar, and also to evaluate the corrosion control of rebar quantitatively. From experimental results, it is found that the nitrite has corrosion inhibition effect, and the Cl^-/NO_2^- of mortar measured after rebar corrosion differ depending on the additive amount of nitrite.

Keywords: calcium nitrite, lithium nitrite, corrosion rebar, chloride ion

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 method. With partial section recovery method (one of the repairing construction method), damaged concrete 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 the corrosion inhibitor cannot be applied to every inch of rebar. On the other hand, in recent years, nitrite has been drawing attention for high protection of corrosion of rebar. In addition, the effect of lithium nitrite has been reported attributed to strength development, deterioration inhibition, and so on (M. TAKAKURA 1988) (T. HORI 1991). Therefore, re-deterioration problem due to the defect of coating of corrosion inhibitor are expected to be solved when using polymer cement mortar with nitrite to section recovery method. However, corrosion control effect of nitrite is not been clear yet. Therefore, in this study, lithium and calcium nitrite are focused upon and experimental examinations were carried out in order to clarify the effects of

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difference between nitrite species and concentration of nitrite in polymer cement mortar. Moreover, the effect of rust protection by nitrite was carried out quantitatively by chloride ion measurement at the rebar positions when the self-potential of rebar decreased below the allowable limit of -350mV for corrosion initiation.

2. EXPERIMENTAL PROGRAM

2.1. Polymer-cement mortar materials

The polymer-cement mortar is composed of fine aggregate, glass and vinylon fibre. Replacement ratio of lithium nitrite in mixing water ("Li-10", "Li-25", "Li-50") of polymer cement mortar was set at 10%, 25% and 50%. "Ca-5", "Ca-10", "Ca-25" polymer cement mortar were made with calcium nitrite replacing mixing water by 5%, 10% and 25% respectively. These mix proportions are shown in Table 1.

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	-	-	-

2.2. Mixing and curing

Polymer cement mortar (here in call "PCM") were prepared with an hand-held electric mixer for 6 minutes on the assumption of real construction, as shown in following process (1)～(3).

(1) Water and lithium or calcium nitrites are added in container.

(2) 30 seconds spent in addition of polymer cement in mixer.

(3) Mixing for 330 second.

One day after casting, specimens were de-molded and cured in atmosphere under 20℃ and relative humidity of 60% during different setting periods of 1 or 28 days.

2.3. Testing of specimens

Flow-table tests were carried out in accordance with JIS R 5201. For salt immersion test, cylindrical specimens of diameter 100mm and length 100mm were used. After 1 or 28 days of curing, specimens were coated with 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"). Corrosion control test of each types of nitrite was carried out using specimens of 40×40×100mm with rebar embedded with cover thickness of 10mm. Specimens were prepared with three samples for each type of mix proportion. After 1 or 28 days of curing, penetration of chloride ion into mortar was done with 10%NaCl solution in a pet bottle set on top of a rebar while specimen is kept setting in atmosphere. Picture 1 shows the specimen setup. Only edge faces were coated by epoxy resin for furnishing sufficient supply of oxygen into mortar. For confirmation of rebar corrosion, natural electric potentials of rebars were measured every three days. In case of a drop of potential below -350mV, chloride content were measured immediately using the cores removed by concrete drill at the sampling range as can be seen in Figure 1.



Picture 1: Shape of specimen for corrosion control

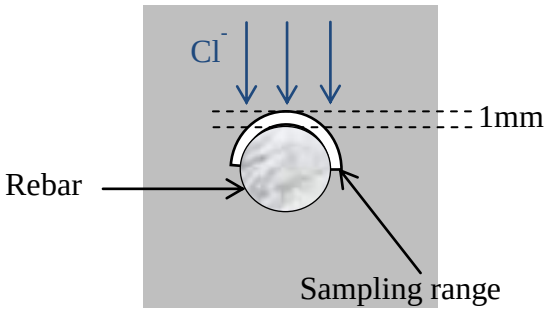

Figure 1: Sampling range

3. RESULTS AND DISCUSSION

Figure 2 shows the flow value in each type of mixing mortar. The flow value clearly decreased with increment of nitrite content, in spite of nitrite type. Focusing attention on different nitrite types, 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 was 0.057mol/l. If more concentration was put in, it was difficult for mixing due to the abnormal setting by the reaction of calcium nitrite with 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 also been reported in other research (A. KITAGAWA1994) (Y.GYOTOKU 2012).

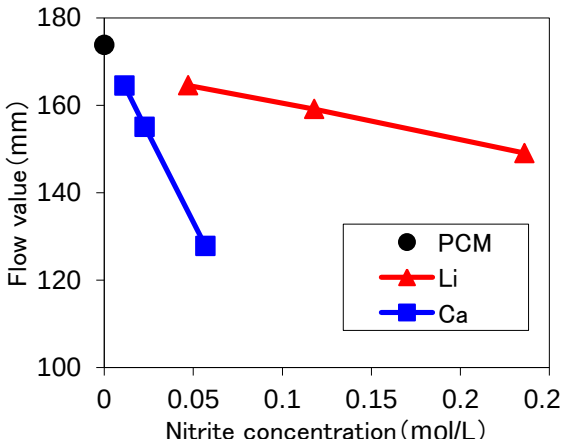

Figure 2: Flow value in each type of mixing mortar

Figure 3 shows the result of apparent chloride ion diffusion coefficient in each type of specimens after 91 days of salt immersion test. The apparent diffusion coefficient of all nitrite specimens was lower than PCM for all curing periods. Comparison between specimens of same concentration of types of nitrites showed that apparent diffusion coefficient has no significant difference between lithium and calcium at 1 day of curing. However, in case of the 28 days curing, lithium has decreased in comparison with calcium. From these result, it was suggested that lithium has some long-term effect on PCM.

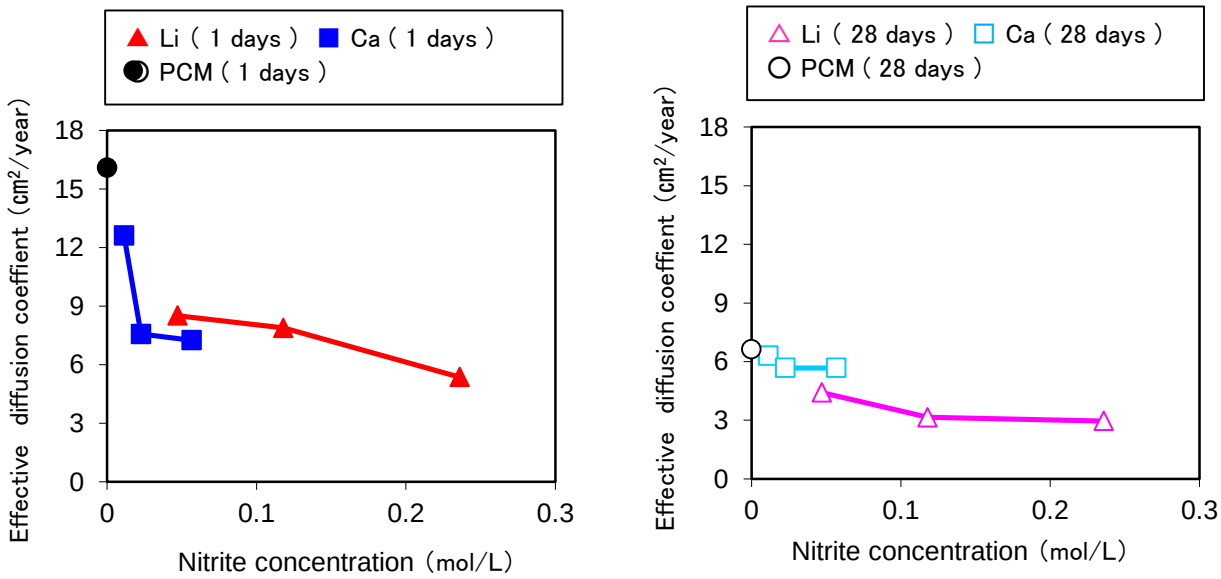

Figure 3: Apparent diffusion coefficient in each type of specimens after 91 days of salt immersion test

Figure 4 shows the natural electric potential of rebar in each type of specimen after 1 day curing. This natural electric potential results are taken as average of 3 specimen, and in case of potentials lesser than -350mV, a single mark is shown (without line) in the graph. At early stages, the natural electric potential decreased below -350mV for lack of oxygen in mortar. Up to the present date, the natural electric potential of PCM in all specimen has been lower than -350mV since 90 days from start of test. And it was confirmed rusting of all rebars due to the chloride ion, as shown in Picture 2. In each of specimens containing nitrite, potential dropped below -350mV at later stages, in comparison with PCM. Focusing attention on difference of nitrite varieties, in case of calcium nitrite, all of the "Ca-0.11", "Ca-0.023" specimens have crossed limit of potential for corrosion initiation (-350mV) after a period of 314 days and 321 days, respectively. And, two specimens of "Ca-0.057" have been confirmed to be rusted in the past. On the other hand, in case of lithium nitrite specimen, all of "Li-0.047", "Li-0.118" potential crossed the -350mV after 373 and 307 day, respectively. Corrosion was confirmed for all rebars.

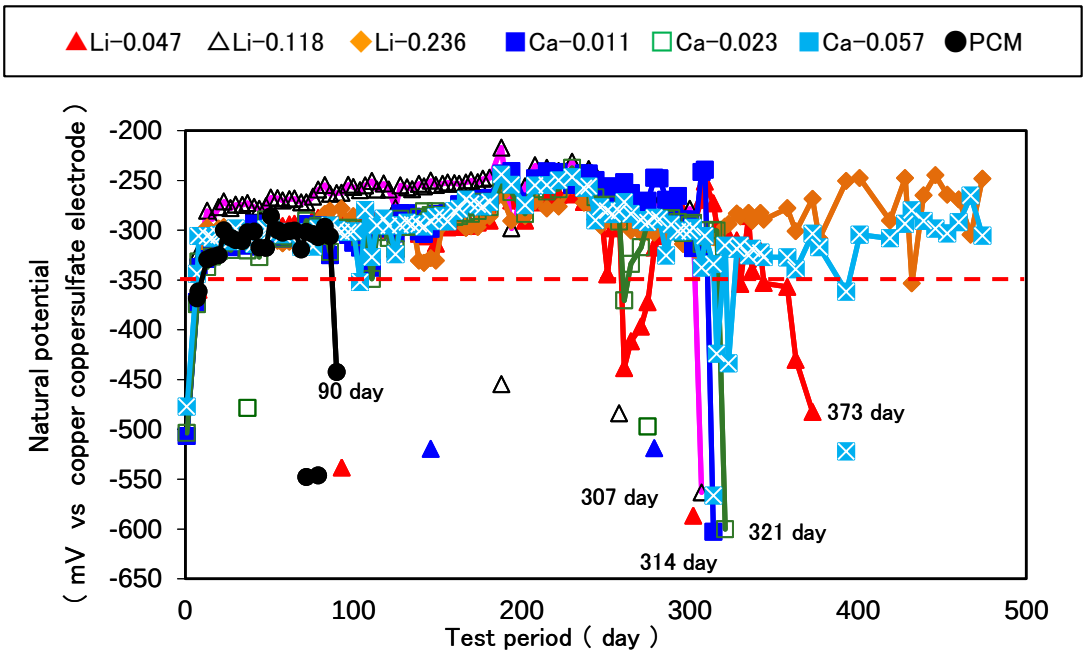

Figure 4: Natural electric potential of rebar in each type of specimen after curing 1 day



Picture 2: Point of corrosion

Figure 5 shows the natural electric potential of rebar in each type of specimen after 28 days of curing. The natural electric potential of PCM in all specimens was lower than -350mV after 119 days from start of test, and corrosion was confirmed in all of rebars. For lithium nitrite specimens, the potential drop below -350mV was observed at later stages when compared to PCM as well as in case of 1 day curing. Currently, all of the "Li-0.047" specimens have crossed the corrosion criteria of -350mV of natural electric potential after a period of 242days, and all rebar were confirmed of corrosion due to the chloride attack. From these results, protection ability was confirmed to increase with increased concentration of nitrite. It suggests that lithium in mortar has high chloride resistance and ability to protect passivation layer.

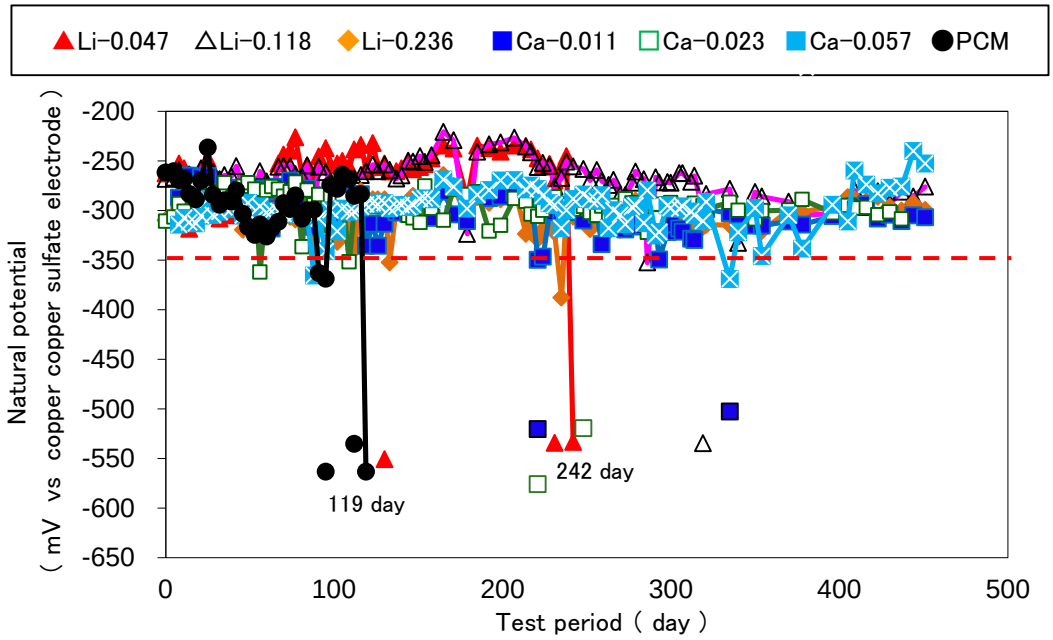

Figure 5: Natural electric potential of rebar in each type of specimen after curing 28day

Figure 6 shows the results of pH in the specimens where corrosion of rebars was confirmed. pH in the specimens are measured using the drilled powder samples (mixing 0.3 g drilled powder with 30g ultra-pure water). As shown in the figure, pH of the specimen tends to decreases with increase of nitrite content. However, specimen confirmed to have corrosion had relatively low concentration nitrite. Also pH of "Ca-0.011", "Ca-0.023", "Li-0.047", "Li-0.188" specimen is almost same. Therefore, protection from rust effect of each nitrite was evaluated by means of the concentration ratio between chloride ion and nitrite ion (Cl^-/NO_2^-).

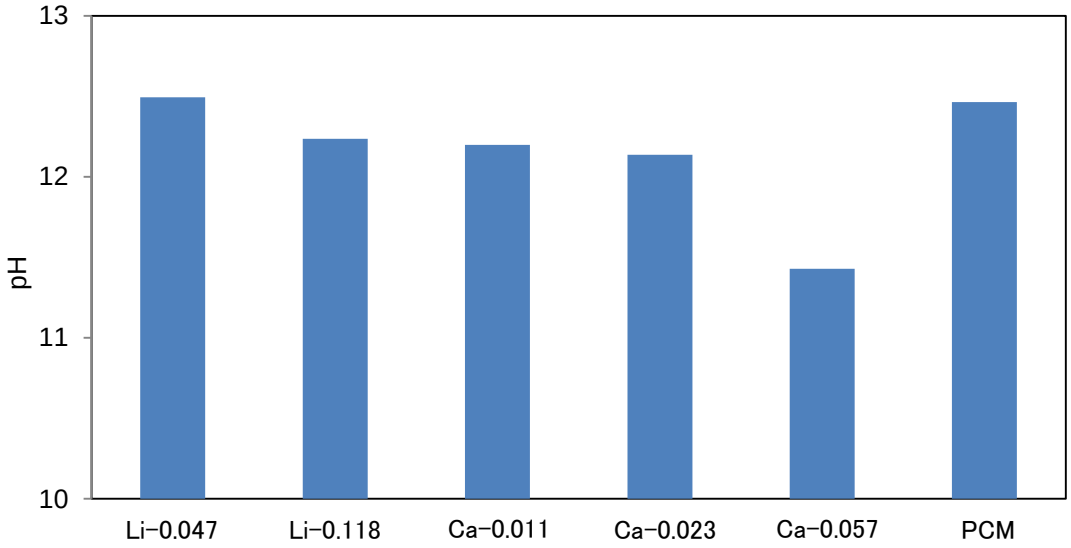

Figure 6: pH in specimens when were confirmed corrosion rebar

Figure 7 shows the Cl^-/NO_2^- of specimens confirmed to have corrosion in rebar. Cl^-/NO_2^- of lithium nitrite were within a range of 0.5, in spite of difference curing time. On the other hand, Cl^-/NO_2^- of calcium nitrite were within a range of 2.1 from 0.3.

Figure 8 shows the relation between concentration of nitrite and Cl^-/NO_2^-. Cl^-/NO_2^- clarified that it decreases with increase of nitrite content, in spite of the kind of nitrite. From these results, it was assumed that water retention ability of lithium nitrite have some effect on the corrosion. In addition, it is reported that the mole fraction of Cl^-/NO_2^- for rust protection vary according to the effect of ionic strength.

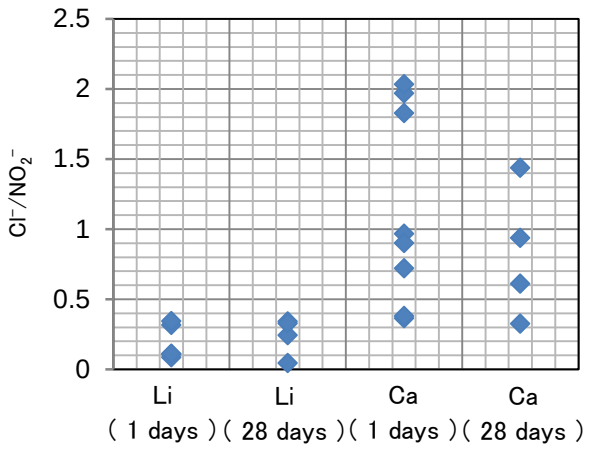

Figure 7: Cl^-/NO_2^- of specimens when confirmed corrosion in rebar

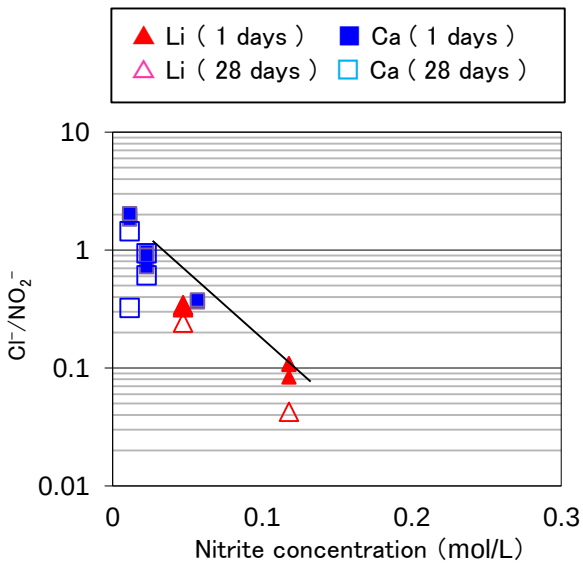

Figure 8: relation concentration of nitrite and Cl^-/NO_2^- when were the corrosion rebar

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 rust protection from different species and concentration of nitrite in polymer cement mortar by discussing the results of salt immersion test and corrosion test.

(1) In case of the addition of lithium nitrite in polymer cement 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 chloride ion penetration into mortar with the increasing use of nitrite. And it is found to prevent potential chloride ion above specified level.

(3) In case of mortar with nitrite, Cl^-/NO_2^- is 0.4～2.1. Cl^-/NO_2^- clarified that it decreases with increase of nitrite content, in spite of the kind of nitrite.

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