Experimental Study of Leaching and Penetration of Nitrite ions in Nitrite-type Repair Materials on the Surface of Concrete

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Abstract

This study aimed to clarify the leaching properties of nitrite ions in nitrite-type repair materials exposed to rainfall. Repaired concrete specimens were prepared for leaching tests using a lithium nitrite solution, and the amounts of leaching and penetration of nitrite ions were measured under simulated rainfall. The results demonstrated that the amount of leaching could be controlled by using polymer cement paste and mortar surface coatings containing lithium nitrite solution, and by using polymer cement mortar surface coatings following direct lithium nitrite solution coatings. Furthermore, the amount of nitrite ion leaching in all cases was lower than the discharge standard value established by the water pollution control law.

Keywords: Nitrite-type repair material, nitrite ion, leaching, penetration, polymer cement mortar, polymer cement paste

1. Introduction

In general, nitrite-type repair materials are commonly used for the purpose of minimizing of corrosion of reinforcements in concrete structures. It is widely known that nitrite ions effectively regenerate passive films on reinforcement surfaces of concrete as they penetrate the surrounding areas [1-3]. However, since nitrite ions easily dissolve in water, there is concern that they can be leached from the surfaces of repair materials upon exposure to rainfall. The aim of this study was to elucidate the leaching properties of nitrite ions in nitrite-type repair materials exposed to rainfall. Repaired concrete specimens were prepared for leaching tests using a lithium nitrite solution, and the amounts of leaching and penetration of nitrite ions were measured under simulated rainfall conditions.

2. Method

The repair methods, which used a 40% water solution composed of lithium nitrite (LN40), are shown in Table 1. These methods are widely used in repair work sites.

The repaired concrete specimen is shown in Fig. 1. The water-cement ratio was 60%. The specimen was demolded one day after casting, cured in water $(20\pm1 \ ^{\circ}C)$ until the age of seven days, and then stored in room-temperature conditions $(20\pm1 \ ^{\circ}C$ and $50\pm5\%$ relative humidity). After curing, the test surface was polished with a sand paper, and cleaned via air-cleaning, and the specimens were repaired using LN40. After repairing, the repaired specimens were cured in room-temperature conditions $(20\pm1 \ ^{\circ}C$ and $50\pm5\%$ relative humidity) for seven additional days. The specimen surfaces excluding test surfaces were coated with an epoxy resin in order to prevent nitrite ion penetration.

The installation conditions of the specimens are shown in Fig. 2. Specimens were installed at a 35° angle and attached to an acrylic plate on the side. In the leaching test, distilled water simulating rainfall was sprayed to the specimen test surfaces. The amount of water sprayed each day was 1.86 g/mm^2 , a value reflecting the av-

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erage annual rainfall in Japan (about 1,700 mm). A wet-dry cycle consisted of one day of spraying and three days of drying, a pattern reflecting the average annual rainfall in Japan (about 128 days). The wet-dry cycle was repeated for one year (91 cycles). Distilled water was sprayed every two hours from 10:00 AM to 4:00 PM on a spraying day. The amount of water sprayed each time was 0.465 g/mm² (a quarter of 1.860 g/mm²). Distilled water flowing down the test

surface was collected after every spraying, and the leached nitrite ion (NO_2^-) concentration was measured using ion chromatography. In the penetration test, distilled water simulating rainfall was sprayed using the same method as the leaching test. However, the NO_2^- concentration in the repair material and repaired concrete was measured at 6 months (45 cycles) and 1 year (91 cycles).

Name of specimen	Repair method	NO_2 solid amount (g)		
		Leaching	Penetration	
N	Non repair	0	_	
LN	Coating of LN40	6.26	0.70	
LNPCP	Surface coating by PCP ^{*1} using LN40 (Thick- ness:2mm)	12.4	1.34	
LNPCM	Surface coating by PCM ^{*2} using LN40 (Thick- ness:5mm)	22.9	2.54	
LN+PCM	Surface coating by PCM ^{*2} after coating of LN40 (Thickness:5mm)	6.26	-	

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*1: Polymer cement paste, *2: Polymer cement mortar

Table 2 Leaching ratio of NO_2^- amount of leaching to NO_2^- solid amount after 91 cycles

Repair method		LN	LN PCP	LN PCM	LN +PCM
NO ₂ ⁻ solid amount in repair material (g)		6.3	12.4	22.9	6.3
After	NO_2^- leaching (g)	1.39	0.52	0.93	0.49
91 cycles	NO ₂ ⁻ leaching ratio (%)	22.2	4.2	4.1	7.8



(a) Leaching test (b) Penetration test Fig. 1 Specimen overview



Fig. 2 Installation conditions of specimens

3. Results and Discussion

The NO_2^- concentration changes found in the leaching test are shown in Fig. 3, and the ratio of NO_2^- amount of leaching to NO_2^- solid amount after 91 cycles is shown in Table 2. The NO_2^-

leaching amount of LN was largest after every cycle, and the leaching ratio of NO_2^- solid amount after 91 cycles was about 22%. The NO_2^- leaching amount of LN+PCM after one cycle decreased by about 70% compared with that of LN. This is because the NO_2^- leaching was controlled by the PCM coating. On the other hand, the NO_2^- leaching amount of LNPCM was larger than that of LNPCP. However, the leaching ratio of NO_2^- solid amount of LNPCM was almost same as that of LNPCP, as shown in Table 2. This implies that there is no actual difference between the leaching properties of LNPCP and LNPCM.

It was confirmed that the NO_2^- concentration in all the repair methods changed at roughly 10 cycles. Afterwards, the change in NO_2^- concentration was small. Although small amounts of NO_2^- were detected, the concentrations of all repair methods after 10 cycles were almost same as that of N (non-repair). Therefore, it is thought that $NO_2^$ hardly leached after 10 cycles for this experimental range of conditions. Considering the discharge standard of the water pollution control law, the NO_2^- leaching amount of all cases in every cycle was smaller than that of the discharge standard value (329 ppm).

The ratio of NO₂⁻ amount of leaching and penetration to NO2⁻ solid amount in repair materials after 91 cycles is shown in Fig. 4. The NO₂⁻ penetration and leaching ratio of LN were about 74% and 22%, respectively. On the other hand, in the case of LNPCP and LNPCM, both addition ratios of the amount of ion penetration in concrete and residual ions in the repair materials were about 90%. Furthermore, both leaching ratios were equal to about 4%. Therefore, it is thought that NO₂⁻ leaching can be controlled using PCP or PCM containing LN40. The total ratios of NO2⁻ amounts of leaching and penetration including residual ions in repair materials were about 93-96%, and there was little difference between NO2⁻ solid amount of repair material and total NO₂⁻ solid amount after 91 cycles. However, the difference was within the range of measurement error of ion chromatography. Therefore, it is thought that the behavior internal and external of NO2⁻ in nitrite-type repair materials was mostly evaluated.



Fig. 3 Change of NO₂⁻ concentration in leaching test

4. Conclusions

The aim of this study was to clarify the leaching properties of nitrite ions in nitrite-type repair materials upon exposure to rainfall. Repaired concrete specimens were prepared using lithium nitrite solution for leaching tests, and the amounts of leaching and penetration of nitrite ions were measured under simulated rainfall. The following conclusions were drawn from the investigation.

- It was confirmed that the NO₂⁻ concentration in all repair methods changed at approximately cycle 10. Subsequent changes in NO₂⁻ concentration were small.
- The NO₂⁻ leaching amounts of all repair methods in all cycles were smaller than that of the discharge standard value.
- The NO₂⁻ leaching can be controlled using PCP and PCM surface coatings with the addition of LN40 and surface coating by PCM after direct coating with LN40.



Fig. 4 Ratio of NO_2^- amount of leaching and penetration to NO_2^- solid amount in repair materials after 91 cycles

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