Laboratory Study on Electrochemical Repair for Reinforced Concrete Exposed to Chloride ions Environment

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Abstract. Due to the “Ring-Anode” effect, reinforced concrete structures will shortly appear to have more serious corrosion deterioration after repairing by conventional rehabilitation methods in a chloride ion environment. Electrochemical repair methods have proved to be an effective and reliable technique for the protection of reinforced concrete structures, especially sacrificial anode cathodic protection (SACP) systems. In the study, active mortars were developed by adding polypropylene (PP) fiber and humectants. Adding PP fiber is intended to control the early shrinkage cracking of the active mortar, and increase the porosity of the active mortar for corrosion products to migrate easily. Using humectants intends to improve resistivity of the active mortar surrounding the anode and performance of the embedded sacrificial anode. The physical and electrochemistry performances of the active mortar were tested compared with the ordinary mortar. In the laboratory, a simulated chloride ions environment was used to evaluate the active mortar with a zinc mesh sacrificial anode for repairing and protecting the reinforcing bar from corrosion in a reinforced concrete column. The tested concrete column was submerged in the salt water and exposed to the air laboratory alternately. According to the criterion of cathodic protection (CP) for reinforced concrete, the reinforcing bars were protected effectively.

1. Introduction

Reinforced concrete structures have many advantages, such as inexpensive and solid. Therefore, they are widely used in many fields, such as marine bridges, harbors and buildings, etc. But it is universal that the reinforced concrete corrodes badly in the chloride ions environment, especially tidal and splash zone due to corrosion of the reinforcing bar, which leads to enormous economic loss. Research and experience has made it very clear that the conventional rehabilitation methods are not adequate remedial actions for this type of deterioration. New corrosion deterioration will appear after repairing shortly due to the “Ring-Anode” effect, which will result in more serious deterioration. The new corrosion cell will occur between the reinforcing bar in the old concrete and that in the patch repair concrete, which is the main reason to accelerate corrosion of the reinforcing bar in the old concrete and cause premature failure of the old concrete. This phenomenon is commonly referred to as “ring anode corrosion” or “halo effect” \cite{1}. The effect of conventional patch repair technology is very poor for these reinforced concrete structures.
At present, many electrochemical methods have been devised to combat corrosion of the reinforcing bar. Cathodic protection (CP) has proved to be an effective and reliable technique for the protection of reinforced concrete structures [2-3]. Especially sacrificial anode CP systems are considered desirable because they create their protective current internally, through a natural reaction wherein the anode corrodes to protect the reinforcing bar. In the study, zinc mesh anode and mortar are composed into a repair and protection system. The system consists of a two-piece stay-in-place fiberglass form with an internal expanded zinc mesh anode, and then it is filled with a Portland cement-sand mortar to repair the deterioration concrete between fiberglass form and concrete base. But the anode stayed in the ordinary Portland cement-sand mortar will be passivation and cannot chronically emit enough protection current. So the filled cement-sand mortar should be having the function to maintain the anode in an electrochemistry active state; at the same time as the surrounding electrolyte of the anode, the cement-sand mortar should have lower resistivity for easy to increase the anode’s current output. This type of cement-sand mortar can be named as active mortar.

So the active mortars were developed by adding PP fiber and humectants in the lab. Adding PP fiber aims to control the shrinkage crack of the active mortar in early [4], so that it can increase the porosity of the active mortar for the anode corrosion products to migrate easily. Using humectants aims to improve resistivity of the active mortar surrounding the anode and performance of the embedded galvanic anode [5]. The physical and electrochemistry performances of the active mortar were tested compared with the ordinary mortar in lab. Then cathodic protection experiment is made on the corrosion reinforced concrete column using zinc mesh sacrificial anode and active mortar in the conditions of chloride ions environment.

2. Experiments

2.1. Materials and Medium

The materials used in the test were 42.5MPa Portland cement, produced by JiangNan cement factory in Jiangsu province; polypropylene fiber, produced by XiaMen building materials Ltd., fiber diameter 18.87um, 12mm long; humectants, LiBr (LB) and LiNO$_3$ (LN) were selected; embedded anode, high-pure zinc was selected; natural sand (delicacy modulus of 2.8). The testing medium was 3.5% sodium chloride (NaCl) water solution.

The diameter and height of the concrete column is 36cm and 85cm separately. The bar reinforcement cage is made by 12 main reinforcing bars and 7 hoop reinforcing bars. The main reinforcements are deformed steel bars with 14mm diameter and 85cm long and the hoop reinforcements are round bar steel with 6mm in diameter.

2.2. Specimen Preparation

The design mix proportions of various mortar specimens are shown on Table 1. The mixed PP fibers were added at a ratio by mass of the mortar; humectants were added to the mix at a ratio of 0.05g to 0.20g of per one cubic centimeter of the mortar. All the mortars were mixed by mixer. Cement, sand and PP fibers were dry prior to adding the water and mixed in mixer for 180 seconds together. If the humectants were added that it should be firstly dissolved in water and the solutions were poured into mixer, and the mortars were mixed for another 180 seconds. Then the mortars specimens were molded. Water cement ratio and the sand ratio of the concrete is 0.6 and 40% separately. The cement is P.II 32.5R Portland cement. In order to accelerate corrosion of the reinforcing bars 1% NaCl (weight percent of the cement) is added in the concrete. The concrete column is cured by covering a wet gunny bag and watering.

A flat zinc mesh anode with 90cm long, 50.5cm wide and 4545cm$^2$ plane areas is used. A layer of special active mortar with 5cm in thickness is applied on the surface of the concrete column and the zinc mesh anode is fixed among the mortar.

During the experiment, the column is submerged in 3.5%NaCl solution and exposed to the laboratory air alternatively. Table 2 is the experiment time and the experiment conditions.
Table 1. Design mix for testing of the mortars

| No. | Water cement ratio | Cement (kg/m³) | Sand (kg/m³) | Water (kg/m³) | LiBr (kg/m³) | LiNO₃ (kg/m³) | PP fiber (%) |
|-----|--------------------|----------------|--------------|--------------|--------------|--------------|--------------|
| K1  | 0.40               | 675            | 1350         | 270          | /            | /            | /            |
| X1  | 0.40               | 675            | 1350         | 270          | /            | /            | 0.10         |
| X2  | 0.40               | 675            | 1350         | 270          | /            | /            | 0.25         |
| X3  | 0.40               | 675            | 1350         | 270          | /            | /            | 0.50         |
| B1  | 0.40               | 675            | 1350         | 270          | 50           | /            | /            |
| B2  | 0.40               | 675            | 1350         | 270          | 100          | /            | 0.10         |
| B3  | 0.40               | 675            | 1350         | 270          | 150          | /            | 0.10         |
| B4  | 0.40               | 675            | 1350         | 270          | 200          | /            | 0.10         |
| N1  | 0.40               | 675            | 1350         | 270          | /            | 50           | 0.10         |
| N2  | 0.40               | 675            | 1350         | 270          | /            | 100          | 0.10         |
| N3  | 0.40               | 675            | 1350         | 270          | /            | 150          | 0.10         |
| N4  | 0.40               | 675            | 1350         | 270          | /            | 200          | 0.10         |

Table 2. Experiment time and the experiment conditions of concrete column

| No. | Time/d | Experiment conditions |
|-----|--------|-----------------------|
| 1   | 30     | (1) The column is submerged in salt solution for 18 hours and exposed to air for 6 hours. (2) The instant-off potentials and 4h depolarization potentials are measured when the column is submerged in salt solution. |
| 2   | 30     | (1) The column is submerged in salt solution for 6 hours and exposed to air for 18 hours. (2) The instant-off potentials and 4h depolarization potentials are measured when the column is exposed to air. |
| 3   | 40     | (1) The column is submerged in salt solution for 6 hours in Tuesday and Thursday separately and exposed to air in other times. (2) The instant-off potentials and 4h depolarization potentials are measured when the column is exposed to air. |
| 4   | 35     | Ditto |
| 5   | 30     | Ditto |

2.3. Testing Procedures

2.3.1. Physical Performance Testing The specimens for the test of compressive strength were cast in the sell mold, measuring 70.7×70.7×70.7mm³. The specimens were demolded after 24 hours and cured in a standard curing room for 28 days. The specimens were taken out and cleaned. The test of resistivity was conducted on each specimen under the dry condition, and then the compressive strengths were tested.

2.3.2. Electrochemistry Performance Testing Zinc anode plate was welded with a copper wire. The exposed area of the anode plate was 3.5cm², and the other areas around the plate were sealed. After the mixed mortars were cast into the said mold and the anode plates were placed into mortars in center. The specimens were demolded after 24 hours and cured in a standard curing room for 14 days. The specimens were taken out and soaked into 3.5% NaCl solution for 24 hours. And then the potentials and potentiodynamic polarization curves of the specimens were tested. The tests were done using a Solartron 1287 Electrochemical Interface controlled by a PC computer. Corr-ware was used to perform the electrochemistry performance testing. All tests were performed in the electrochemical cells composed of three electrodes, which is a working electrode (zinc anode
plate), a counter-electrode made of platinum, and a saturated calomel reference electrode (SCE). The tests were from open potential and the scan speed was set at 0.5mV/s.

3. Results and Analysis

3.1. Compressive Strength and Resistivity of Mortar

The test results of 28 days compressive strength and the resistivity of different mix mortars are shown in Figure 1 and Figure 2.

![Figure 1. Comparison with 28d compressive strength of the mortar specimens](image1)

![Figure 2. Comparison with 28d resistivity of the mortar specimens](image2)

Compared with the control specimen (K1), it was observed that the compressive strength of specimens (X1, X2, and X3) degraded with the added PP fibers increasing in Figure 1. It is due to the increase of porosity of the mortar.

It was observed that the resistivity of mortars (X1, X2, and X3) reduced in Figure 2 when the PP fibers were mixed, which is benefit to dispersion of cathodic protection current. But the resistivity of the mortars became larger with the enhancement of PP fibers. It is shown that added more PP fibers make against to the lower resistivity and higher compressive strength of the mortar specimens. Moreover it is found the mortars become difficulty to mix along with the increase of PP fibers, so the ratio of 0.1% PP fibers was selected in the followed test specimens.

In Figure 1, it was observed that the compressive strength of all the specimens containing the humectants were at least 12% smaller than that of the No. X1 specimen without added the humectants. So the addition of humectants could significantly reduce the compressive strength of the mixed mortar and the strength reduced with the enhancement of the added humectants. It is not benefit to the active mortars as repairing materials, so the humectants should not be added more considering the compressive strength.

The resistivity of the specimens evidently reduced and became smaller with the enhancement of the humectants, which is very benefit to reduce the loop resistivity of CP systems. Added more humectants are useful for the resistivity of the active mortars. So it is necessary to do more tests to determine how much the humectants should be added.

3.2. Open Potential of Zinc Anode in Mixed Specimens

The test results of zinc anode open potential in the mixed specimens are shown in Figure 3.

Open potential of zinc anode was only -606 mV (vs. SCE) in the control specimen, so the zinc anode had been passivation and could not emit current in the ordinary mortar. Open potentials of zinc anode in the others specimens were nearly or more than -1000mV, and the open potentials would become more negative with the increase of the added humectants. Compared with the two humectants, the zinc anode in the specimens added LB was more negative than that added LN at the same mixed quantity.
3.3. Potentiodynamic Polarization Curves of Zinc Anode in Mixed Specimens

Potentiodynamic polarization curves of zinc anode in the specimens mixed with LB and LN are respectively presented in Figure 4 and Figure 5.

From Figure 4 and 5, it can be known that both humectants are helpful for the zinc anode to emit current in mortar specimens. When the two humectants were respectively added in the same quantity, it is obvious that zinc anode can emit more current in mortar specimens mixed with LB. But if the humectant of LB was used too much, this will result in an additional expense and the anode will be in passivation state. So the added quantity of LB should not be too much, and humectant of LB is more effective for the zinc anode to increase the protective current delivered to the reinforcing bar in the mortar chronically. These are accordant with other relative study [6-7].

3.4. Concrete Column Protection Experiment

The concrete column is put in a plastic box with 80cm long, 60cm width and 90cm height. The experiment is made by connecting the zinc mesh and the reinforcing bars of the concrete with cables. Current output of the zinc mesh sacrificial anode and the polarization potentials of the reinforcing bars are measured, polarization decay of the reinforcing bars are calculated, and the protection effects of the reinforcing bars are estimated according to the criterion of cathodic protection for reinforced concrete. The potentials are measured by saturated calomel electrode.
the results of the five experiments are very similar.

Table 3. Current outputs and densities of the zinc mesh anode and cathodic protection densities

| No. | Current outputs of the zinc mesh anode (mA) | Current output densities of the zinc mesh anode (mA/m²) | Cathodic protection densities (mA/m²) |
|-----|---------------------------------------------|--------------------------------------------------------|-------------------------------------|
|     | Maximum | Minimum | Mean | Maximum | Minimum | Mean | Maximum | Minimum | Mean |
| 1   | 6.0     | 3.4     | 4.1  | 13.2    | 7.5     | 9.0  | 10.5    | 6.0     | 7.2  |
| 2   | 4.8     | 2.9     | 4.1  | 10.6    | 6.4     | 9.0  | 8.4     | 5.1     | 7.2  |
| 3   | 5.6     | 2.8     | 3.8  | 12.3    | 6.2     | 8.4  | 9.8     | 4.9     | 6.7  |
| 4   | 7.1     | 3.9     | 4.5  | 15.6    | 8.6     | 9.9  | 12.4    | 6.8     | 7.9  |
| 5   | 6.0     | 3.7     | 4.2  | 13.2    | 8.1     | 9.2  | 10.5    | 6.5     | 7.4  |

In the study five depolarization tests are made. Table 4 is the results of instant off potentials and 24h depolarization potentials of the reinforcing bars measured at various measurement points, and the calculation results of the polarization decay. Values of 24h polarization decay of the five experiments are between 121mV and 336mV. The instant off potentials of the five experiments are between -831mV and -998mV. They all satisfy the requirement of the EN12696[9]: 2000. It is shown that the reinforcing bars in concrete are protected effectively.

Table 4. Measured results of instant off potentials and calculation results of polarization decay

| Measurement Location | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 |
|----------------------|-------|-------|-------|-------|-------|
| Top 1                | 998   | 839   | 159   | 907   | 665   |
| Middle 1             | 998   | 839   | 159   | 949   | 731   |
| Low 1                | 998   | 839   | 159   | 999   | 795   |
| Top 2                | 995   | 840   | 155   | 908   | 787   |
| Middle 2             | 995   | 840   | 155   | 955   | 877   |
| Low 2                | 995   | 840   | 155   | 975   | 848   |
| Top 3                | 995   | 838   | 157   | 881   | 720   |
| Middle 3             | 995   | 838   | 157   | 944   | 773   |
| Low 3                | 995   | 838   | 157   | 970   | 781   | 189   | 955   | 764   | 191   | 905   | 666   | 239   | 915   | 634   | 281   |

①-- Instant off potentials, unit is -mV; ②--24h depolarization potentials, unit is -mV; ③--Polarization decay, unit is mV.

4. Conclusions

Compressive strength of the active mortar reduces with the addition of PP fibers; adding humectants will markedly reduce the compressive strength of the active mortars. Resistivity of the active mortars reduces when the PP fiber is used, but the resistivity will augment with increasing of PP fiber. Adding humectants are very useful for reducing the resistivity of the active mortars.

The electrochemistry performance of the active mortar is obviously improved by adding the
humectants, and both two humectants are helpful for the current output of the zinc anode in the mortars. Lithium bromide is more effective for the zinc anode to emit current in the active mortar chronically, but the added quantity of LB should not be mixed too much. The researched active mortar and zinc mesh anode can effectively protect the reinforcing bars from corrosion in concrete column which is submerged in the salt water and exposed to the air laboratory alternately.

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