

## Corrosion resistant performance of a chemical quenched rebar in concrete

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### ABSTRACT

The corrosion resistance performance of the rebar quenched by a new chemical reagent FM in concrete containing chloride ions was evaluated comparing with bare rebar, water-cooled rebar and air-cooled rebar using electrochemical methods. Two different accelerated corrosion tests (14 cycles of dry/wet alternated corrosion tests and long-term immersion tests) were carried out to accelerate the corrosion process. EIS results of both accelerated corrosion tests showed the corrosion resistance performance of different rebar specimens could be sequenced from high to low as FM-cooled rebar, bare rebar, air-cooled rebar, and water-cooled rebar. It was observed that, after 14 cycles of accelerated corrosion tests, the corrosion degree of FM-cooled rebar is the slightest and most of the initial scale remains undamaged. This result proves that the corrosion resistance of the FM-cooled rebar is much better than the other three kinds of rebar. By using FM-cooling process, the corrosion resistance performance of rebar in concrete has been improved by optimizing the quality of the scale.

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### 1. Introduction

Rebar is widely used as the skeleton of reinforced concrete in construction industry. The corrosion resistance performance of rebar includes two aspects. One is the corrosion resistance of rebar in atmosphere during storage and transportation, and the other is the corrosion resistance of rebar in reinforced concrete [1–4].

To improve the atmospheric corrosion resistance of rebar, a new type of quenching medium named FM has been developed. It was used as the quenching medium during cooling of the hot-rolled rebar instead of water. A compact scale forms on the surface of the rebar when using FM-cooling, which provides a better protective performance against corrosion than the water-cooled and air-cooled rebar [5,6]. However, when the FM-cooled rebar serves in concrete, it is also expected to provide better corrosion performance.

Corrosion of rebar in concrete attracts great attention because it causes structure degradation of the reinforced concrete. The rust formed on the rebar surface may cause a volume expansion, which will generate a tensile stress within the surrounding concrete. The stress will cause cracks and spalling of the concrete cover, and eventually leads to the failure of the concrete structure. As the corrosion of rebar in concrete occurs on the rebar surface, the surface state of the rebar (such as the stability, the compactness and the thickness of the surface film) affects the corrosion resistance greatly. At present, the main kinds of rebar used in concrete include bare rebar, scaled rebar and rusted rebar. Generally, a passive film consisting of a compact  $\text{Fe}_3\text{O}_4$  and/or  $\text{Fe}_2\text{O}_3$  layer [7,8] or  $\gamma\text{-}$

$\text{FeOOH}$  layer [9,10] can form on the surface of bare rebar due to the high alkalinity condition (pH 12.5–13.5) of the pore solution in concrete. This film can protect the rebar against corrosion. However, this passive state can be destroyed by aggressive ions (chloride, sulfate) or by an acidification of the environment close to the rebar (carbonation) [11–13]. Moreover, the thickness of the passive film formed on bare rebar is only tens of Å [14–16]. Therefore, it can be easily destroyed and its protection action against corrosion is limited. The corrosion rate of rusted rebar in concrete is very high even without chloride [17]. As for scaled rebar, the scale consists of  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  [18–20]. The thickness of the scale is about 20  $\mu\text{m}$ , which helps improve the corrosion resistance. However, since the structures of oxide scale are different with different cooling processes (such as water-cooling, air-cooling and FM-cooling), the corrosion resistances of the scale is also distinct from each other [5]. Therefore, the corrosion resistance of rebar can be improved by improving the quality of the surface scale.

In the present work, the corrosion resistant performance of the FM-cooled rebar was evaluated comparing with bare rebar, water-cooled rebar and air-cooled rebar in concrete containing chloride ions.

### 2. Experiments

#### 2.1. Materials and procedures

##### 2.1.1. Rebar samples preparation

The steel used in the experiment was a commercial 20SiMn hot-rolled rebar. The chemical composition (wt.%) is: C 0.17–0.25, Si 0.40–0.80, Mn 1.20–1.60, P 0.050, S 0.050. The rebar samples were machined into cylinders ( $\Phi 10 \text{ mm} \times 60 \text{ mm}$ ) and the surfaces were polished using 1200# sand paper. The preparation processes of four different surface states (bare, with water-cooled scale,

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with air-cooled scale and with FM-cooled scale) are as follows. The machined samples were used as bare rebar directly. For the other three kinds of rebar, the machined samples were heated to 1000 °C for 10 min in the pipe furnace under an anti-oxidizing flux protection. Then the high temperature samples were cooled by water, air and chemical reagent FM, respectively. The quenching time is about 1 s for both water-cooling and FM-cooling processes and then the samples were cooled in air to the room temperature. The component of FM is:  $\text{H}_2\text{O}_2$  10%,  $\text{NaBO}_3$  5 g/l,  $\text{Na}_2\text{SiO}_3$  0.45 g/l,  $\text{MgSO}_4$  0.45 g/l, in which  $\text{H}_2\text{O}_2$  acts as oxidant and the other reagents act as stabilizing agents.

### 2.1.2. Mortar samples preparation

Reinforced mortar samples (80 mm in diameter and 80 mm in height) were cast according to standard experimental procedures using ordinary Portland cement 42.5 (with a water/cement ratio of 0.5 and cement/sand ratio of 1/3). The schematic diagram of the electrode system is shown in Fig. 1, and all the length units are in millimeter. A two-electrode cell was employed. The working electrodes (WE) were

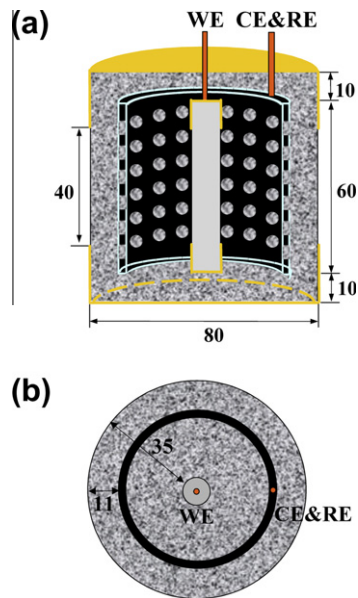


Fig. 1. Schematic diagram of the electrode system for reinforced mortar samples. (a) Side sectional view, (b) top sectional view.

four kinds of rebar with different surface states. Both ends of the rebar were coated with epoxy resin, leaving an exposed length of 40 mm. The rebar was positioned at the center of the mortar sample with a cover thickness of 35 mm. In order to achieve a uniform distribution of the electric-power line, an annular graphite electrode of 60 mm height was used as the counter electrode (CE) and the reference electrode (RE). It was positioned with the cover thickness of 11 mm. After demoulding at 1 day, the mortar samples were cured in a standard curing chamber at  $20 \pm 1$  °C and  $\geq 95\%$  RH for 28 days. Then both ends of the mortar samples were coated with epoxy resin leaving an exposed height of 40 mm profile to avoid the non-uniform penetration of solution.

## 2.2. Accelerated corrosion tests

### 2.2.1. Dry/wet cyclic corrosion tests

Fourteen cycles of severe dry/wet cyclic corrosion tests were carried out to accelerate the corrosion of rebar in mortar. Before the cyclic tests, the samples were immersed in de-ionized water for 1 day which was referred as cycle 0. The cyclic condition of each cycle is drying at 80 °C for 4 days in a drying cabinet and immersing in 3.5% NaCl solution for 1 day.

### 2.2.2. Long-term immersion tests

Long-term immersion tests were also carried out to accelerate the corrosion of rebar in mortar. Firstly, the mortars containing four kinds of rebar were immersed in de-ionized water to reach a constant weight, then immersed in 3.5% NaCl solution and carried out the electrochemical measurements.

## 2.3. Electrochemical measurements

The Electrochemical Impedance Spectroscopy (EIS) measurement was carried out over a frequency range of 100 kHz–10 mHz and a amplitude sinusoidal voltage of 10 mV when the mortars are in 3.5% NaCl solution, using a PAR 273 potentiostat and a PAR 5210E lock-in amplifier. During the dry/wet cyclic corrosion tests, EIS was measured after each dry/wet cycle. During the long-term immersion tests, EIS was measured at different immersion time. All the measurements were carried out at room temperature (25 °C).

## 3. Results and discussion

### 3.1. The appearance morphology of four rebar after dry/wet cyclic corrosion test

As the volume expansion caused by rust formation can destroy the initial surface film, the breakage degree of the initial surface film can reflect the corrosion degree. Fig. 2a–d showed the appear-

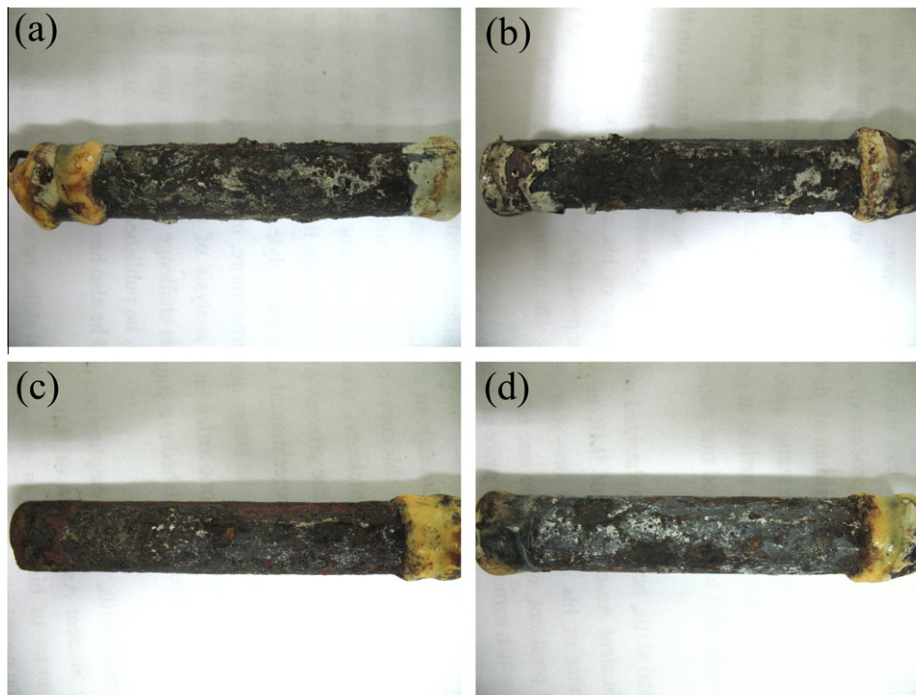


Fig. 2. Appearance morphology of corrosion products. (a) Bare rebar, (b) water-cooled rebar, (c) air-cooled rebar, (d) FM-cooled rebar.

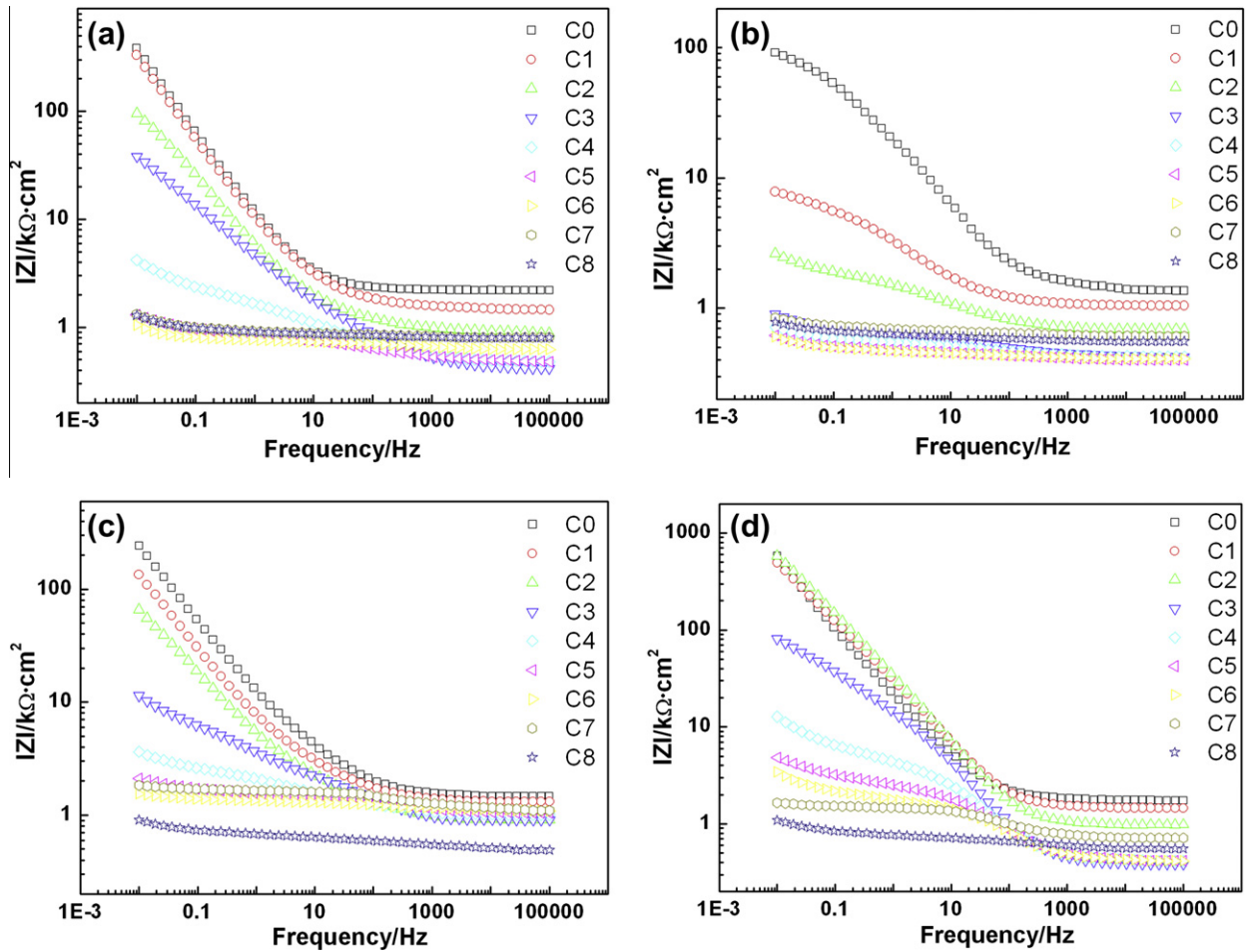


Fig. 3. Impedance modulus plots for four rebar in mortar as a function of dry/wet cycles. (a) Bare rebar, (b) water-cooled rebar, (c) air-cooled rebar, (d) FM-cooled rebar.

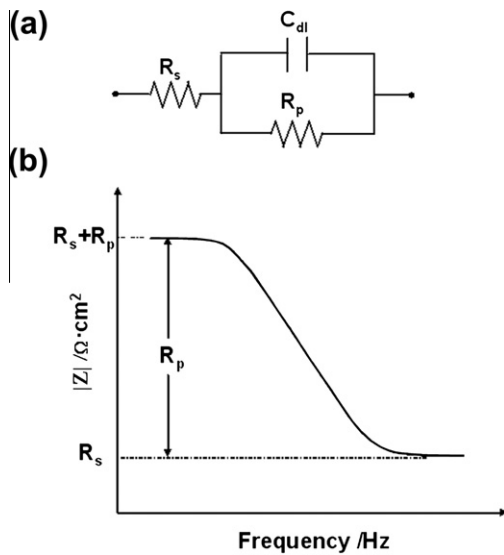


Fig. 4. Schematic diagram of a simple electrochemical electrode system. (a) Equivalent circuit, (b) modulus plot of EIS spectra.

ance morphologies of four kinds of rebar after 14 cycles of dry/wet cyclic corrosion test. The surfaces of both bare rebar and water-cooled rebar (Fig. 2a and b) appeared scraggy and covered by rust, which indicates the rebar was severely corroded. Although the surface of air-cooled rebar (Fig. 2c) appeared smoother than bare re-

bar and water-cooled rebar, most of the outer rust layer has broken off due to the volume expansion caused by rust formation. However, the surface of FM-cooled rebar (Fig. 2d) appeared relatively smooth and most of the initial scale remains well, which indicates the corrosion degree is minimal.

### 3.2. EIS spectra of dry/wet alternated test

Fig. 3a–d shows the impedance modulus plots of four rebar specimens with different scale in mortar, in which c0 corresponds to the initial state, and c1–c8 correspond to the former eight dry/wet cycles of accelerated corrosion test. As the changes of EIS spectra are negligible after the eighth cycle, those results are omitted in this discussion.

According to the electrochemical theory [21], a simple electrochemical electrode system may be described by an equivalent circuit (as shown in Fig. 4a), in which  $R_s$  represents the solution resistance;  $C_{dl}$  represents the capacitance of the electric double layer; and  $R_p$  represents the polarization resistance caused by charge transfer reaction. Fig. 4b shows the modulus plot of EIS spectra corresponding to Fig. 4a. The  $R_s$  corresponds to the highest frequency impedance, and  $R_s + R_p$  corresponds to the lowest frequency impedance. In the case of rebar embedded in concrete, because the rebar was covered by different scale,  $R_p$  consists of film resistance ( $R_f$ ) and charge transfer resistance ( $R_{ct}$ ) [22]. The protective performance of scale can thus be described by  $R_p$ .

As for the impedance spectra measured in this experiment, the value of impedance modulus at frequency of 10 kHz is assumed

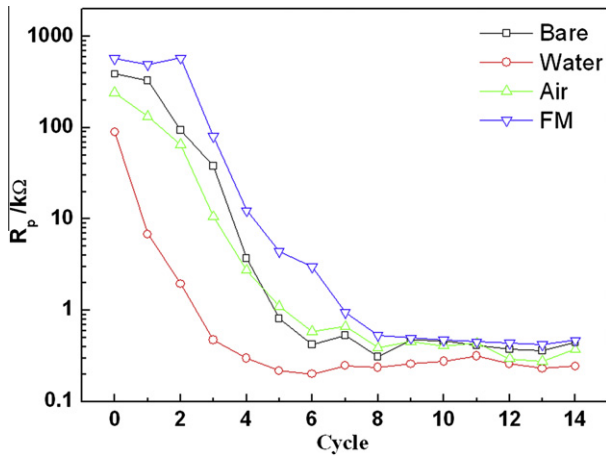


Fig. 5. Evolution of  $R_p$  as a function of dry/wet cycles for four rebar.

equal to  $R_s$ , and the value of impedance modulus at frequency of 10 mHz is assumed equal to the sum impedance of  $R_s + R_p$ . Consequently,  $R_p$  can be calculated. The results are shown in Fig. 5. During the first several cycles,  $R_p$  of all kinds of rebar decreases with the increase of dry/wet cycles. The decrease of  $R_p$  indicates the increase of corrosion rate and the degradation of scale. During the last several cycles, the values of  $R_p$  of all kinds of rebar keep constant. This implies the rebar were corroded at a certain corrosion rate.

Comparing the value of  $R_p$  of the four rebar, the sequence of  $R_p$  at cycle 0 is: FM-cooled rebar > bare rebar > air-cooled rebar > water-cooled rebar. Therefore, the corrosion resistance of scale formed by FM-cooling is the best among the four rebar. Furthermore, the degradation rate of  $R_p$  also differs significantly.  $R_p$  of water-cooled rebar decreases rapidly since the first cycle, and it reaches the minimum at the fourth cycle. For air-cooled rebar and bare rebar,  $R_p$  decreases obviously from the first cycle and the second cycle, respectively, and it reaches the minimum at the sixth cycle. However, for FM-cooled rebar, the  $R_p$  decreases from the third cycle, and it reaches the minimum at the eighth cycle. Therefore, the degradation rate of  $R_p$  of FM-cooled rebar is the slowest, which indicates the protection performance of scale formed by FM-cooling against corrosion is the best.

3.3. EIS spectra of long-term immersion test

Fig. 6a–d shows the impedance modulus plots of the four rebar specimens in mortar immersed in 3.5% NaCl solution for different immersion time.  $R_p$  can be calculated by the same means as in the dry/wet cyclic tests. Fig. 7 shows the evolution of  $R_p$  with immersion time for the four rebar. The values of  $R_p$  of the four rebar decreases with the increase of immersion time, which indicates the increase of corrosion rate. However, the value of  $R_p$  differs significantly for the four rebar. The sequence of  $R_p$  is: FM-cooled rebar > bare rebar > air-cooled rebar > water-cooled rebar. Moreover, the value of  $R_p$  of water-cooled rebar is only about 12 kΩ during initial period of immersion, which is only several

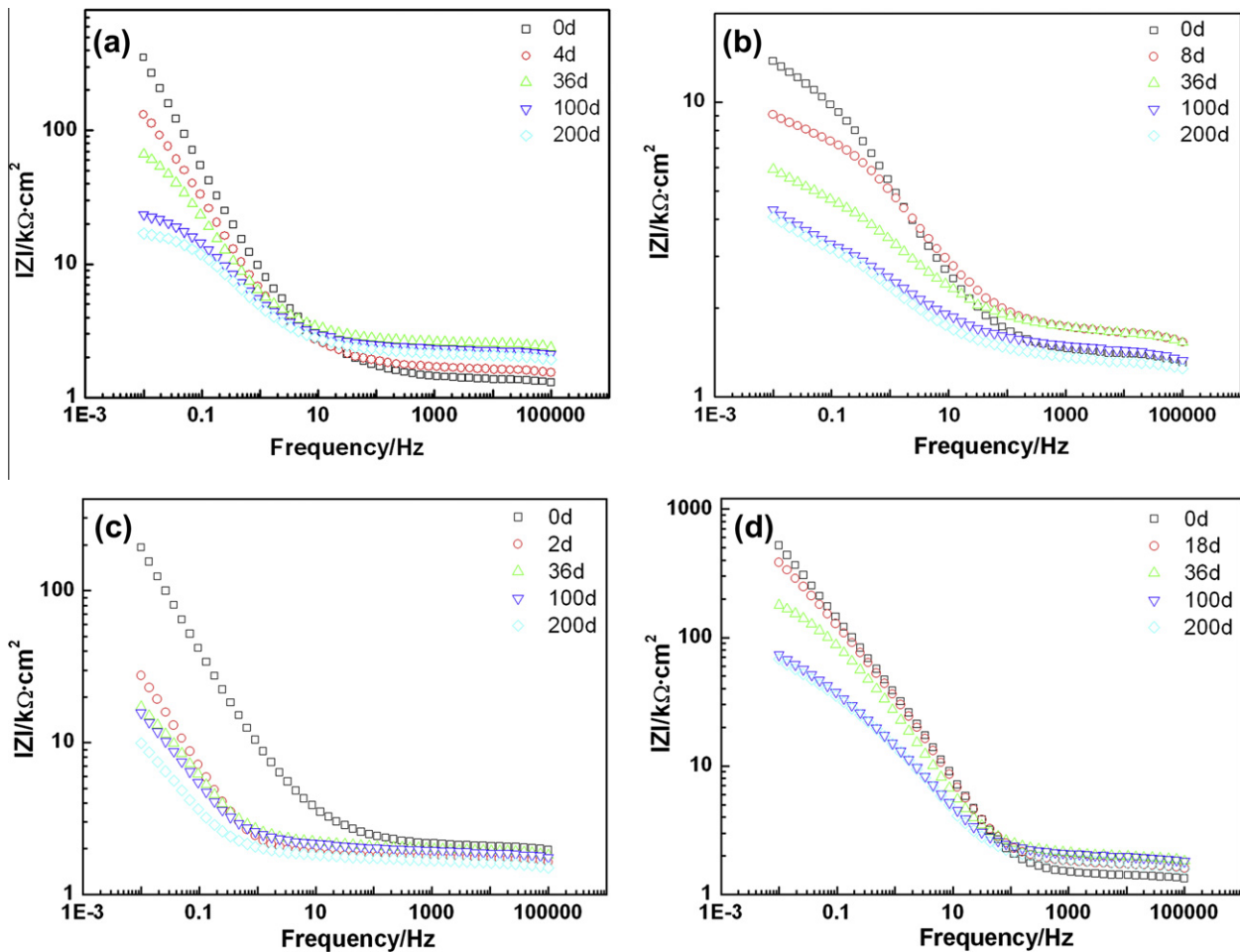


Fig. 6. Impedance modulus plots for four rebar in mortar as a function of immersion time. (a) bare rebar, (b) water-cooled rebar, (c) air-cooled rebar, (d) FM-cooled rebar.

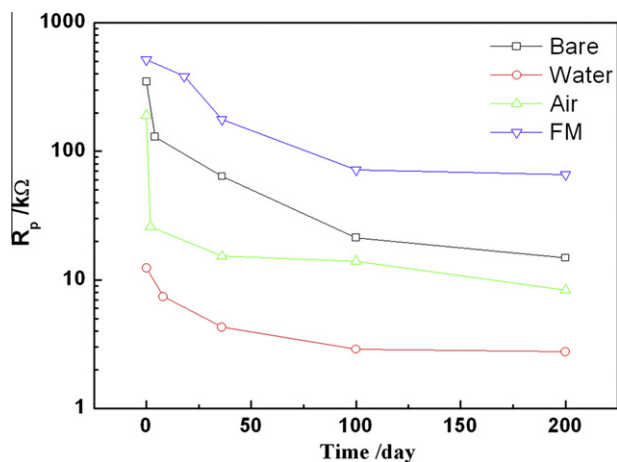


Fig. 7. Evolution of  $R_p$  with immersion time for four rebar.

centesimal compared to the other three rebar. As for the bare rebar and air-cooled rebar,  $R_p$  decreases significantly from the early several days. This indicates that the degradation of the surface film and the increase of the corrosion rate occur quickly at the early immersion period. However, the value of  $R_p$  of FM-cooled rebar is the largest, and it decreases slowly with the immersion time. Therefore, the corrosion rate of FM-cooled rebar is the slowest, and the protection performance against corrosion of scale formed by FM-cooling is the best.

According to the above results, it can be summarized that the corrosion resistance performance of FM-cooled rebar is much better than the other three kinds of rebar. As the breakdown of the surface film will accelerate the corrosion of rebar, the quality of the surface film influences the corrosion resistance performance of rebar.

As mentioned above, in high alkaline concrete without chloride ions, a compact passive layer will form on the surface of bare rebar. However, as the passive film on the bare rebar is very thin, it will be easily destroyed by chloride ions. Thus, the corrosion on bare rebar is fast and severe. The compositions and structure of scale on the other three kinds of rebar have been analyzed in the previous study [6]. The results show that the scale on all three kinds of rebar consists of FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, but the relative content of oxides is different. The relative content of Fe<sub>3</sub>O<sub>4</sub> is close to 60% when using FM-cooling; however, the Fe<sub>3</sub>O<sub>4</sub> content is only about 40% for water-cooled and air-cooled rebar. As Fe<sub>3</sub>O<sub>4</sub> is the leading factor contributing to the corrosion resistance of the scale among these three oxides due to its stable electrochemical property and compact inverse spinal structure, the corrosion resistance of FM-cooled rebar is the best. Moreover, the structures of the scale on three kinds of rebar also differ from each other. The scale of water-cooled and air-cooled rebar is porous, thus, the aggressive ions can penetrate through the pores to the substrate and induce corrosion. However, the scale on the FM-cooled rebar is compact and it is much thicker than the passive film on bare rebar. Therefore, the FM-cooled scale is more beneficial to resisting corrosion.

#### 4. Conclusions

1. After 14 cycles of dry/wet alternated corrosion test, the corrosion degree of FM-cooled rebar is the slightest and most of the initial scale remains undamaged, which proves that the corrosion resistance of the FM-cooled rebar is much better than the other three kinds of rebar.
2. In both the dry/wet cyclic corrosion test and the long-term immersion test, the sequence of corrosion resistance performance of rebar reflected from EIS spectra is FM-cooled rebar > bare rebar > air-cooled rebar > water-cooled rebar.
3. Applying the FM-cooling process, the corrosion resistance performance of rebar in concrete has been improved by optimizing the quality of the scale.

#### References

- [1] Almusallam AA. Effect of degree of corrosion on the properties of reinforcing steel bars. *Construct Build Mater* 2001;15(8):361–8.
- [2] Zitrou E, Nikolaou J, Tsakiridis PE, Papadimitriou GD. Atmospheric corrosion of steel reinforcing bars produced by various manufacturing processes. *Construct Build Mater* 2007;21:1161–9.
- [3] Kumar V. Protection of steel reinforcement for concrete-A review. *Corros Rev* 1988;16(4):317–58.
- [4] Elsener B. Corrosion rate of steel in concrete-measurements beyond the Tafel law. *Corros Sci* 2005;47:3019–33.
- [5] Wei J, Dong JH, Han EH, Ke W. Study on the corrosion resistance of hot rolled rebar quenched with a new chemical reagent. *Corros Sci Protect Technol* 2009;21(5):468–71.
- [6] Wei J, Dong JH, Ke W. The influence of cooling processes on the corrosion performance of the rebar scale. *Construct Build Mater* 2010;24:275–82.
- [7] Nagayama M, Cohen M. The anodic oxidation of iron in a neutral solution I. The nature and composition of the passive film. *J Electrochem Soc* 1962;109:781–90.
- [8] Kruger J, Calvert JP. Ellipsometric-potentiostatic studies of iron passivity. *J Electrochem Soc* 1967;114:43.
- [9] Oranowska H, Szklarska-Smialowska Z. An electrochemical and ellipsometric investigation of surface films grown on iron in saturated calcium hydroxide solutions with or without chloride ions. *Corros Sci* 1981;21:735.
- [10] Zakroczyński T, Fan C-J, Szklarska-Smialowska Z. Kinetics and mechanism of passive film formation on iron in 0.05M NaOH. *J Electrochem Soc* 1985;132:2862–7.
- [11] Moreno M, Moms W, Alvarez MG. Corrosion of reinforcing steel in simulated concrete pore solutions-effect of carbonation and chloride content. *Corros Sci* 2004;46(11):2681–99.
- [12] Morris W, Vazquez VM. Corrosion of reinforced concrete exposed to marine environment. *Corros Rev* 2002;20(6):469–508.
- [13] Martin FJ, Olek J. Experimental procedure for fundamental studies of reinforcing steel corrosion processes. *Rev Sci Instrum* 2003;74(4):2512–6.
- [14] Kudo K, Shibata T, Okamoto G, Sato N. Ellipsometric and radiotracer measurements of the passive oxide film on Fe in neutral solution. *Corros Sci* 1968;8(11):809–14.
- [15] Revie RW, Baker BG, Bockris JO'M. The passive film on iron: an application of auger electron spectroscopy. *J Electrochem Soc* 1975;122(11):1460–6.
- [16] William EO'G. Mössbauer study of the passive film on iron. *J Electrochem Soc* 1980;127(3):555–63.
- [17] Novak P, Mala R, Joska L. Influence of pre-rusting on steel corrosion in concrete. *Cem Concr Res* 2001;31:589–93.
- [18] Pfeil LB. The constitution of scale. *J Iron Steel Inst* 1931;123:237–55.
- [19] Sun W, Tieu AK, Jiang Z, Lu C, Zhu H. Surface characteristics of oxide scale in hot strip rolling. *J Mater Process Technol* 2003;140:76–83.
- [20] Burke DP, Higginson RL. Characterization of multi-component scale by electron back scattered diffraction (EBSD). *Scripta Mater* 2000;42:277–81.
- [21] Cao Ch N, Zhang JQ. Introduction of electrochemical impedance spectra. Beijing: Science; 2002. p. 37–44.
- [22] Mansfeld F. Electrochemical Impedance Spectroscopy (EIS) as a new tool for investigating methods of corrosion protection. *Electrochim Acta* 1990;35(10):1533–44.