

# Study on the critical molar ratio of corrosion resistance of concrete under the coupling action of carbonation and chloride

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**Key words:** carbonization, chlorine salt, potential, critical molar ratio

**Abstract:** By chlorine salt and carbonization under the combined action of simulated concrete pore solution in determination of the natural potential of the reinforced method of the influence of basicity of chloride contaminated concrete critical  $\text{NO}_2^-/\text{Cl}^-$  molar ratio. Results show: The increase of pH value or  $\text{NO}_2^-/\text{Cl}^-$  molar ratio in concrete simulated pore solution can inhibit the corrosion of reinforcing steel bar; The  $\text{NO}_2^-/\text{Cl}^-$  molar ratio of molar ratio less than the critical  $\text{NO}_2^-/\text{Cl}^-$  mole ratio of the actual concrete is suppressed in the concrete simulated pore solution; The pore solution simulation has the concrete carbonization, corrosion inhibition required  $\text{NO}_2^-/\text{Cl}^-$  molar ratio is 3 times of ordinary concrete carbonation.

## Introduction

At present, the main components of the anti rust agent are nitrite<sup>[1]</sup>. Some domestic research shows that: In concrete with chlorine salt, when the  $\text{NO}_2^-/\text{Cl}^-$  molar ratio is greater than 1.2 completely inhibit the corrosion of steel<sup>[2]</sup>. For the corrosion caused by carbonation, when the content of nitrate in concrete is 1.66% of cement mass, the corrosion of steel can be completely inhibited<sup>[3]</sup>. And for both chlorine salt and carbide composite deterioration of concrete in inhibiting corrosion of reinforcement required for nitrite content of research has not been reported. According to the research results of Hausmann<sup>[4]</sup>, the corrosion of steel bars is closely related to the  $\text{Cl}^-/\text{OH}^-$  of the solution, that is to say, the chloride ion and alkalinity can influence the corrosion of steel bar. And cement varieties, the degree of carbonation of concrete will change the pH value of the pore solution. So it is not only to study the anti corrosion effect of nitrite on the concrete, but also to consider the  $\text{NO}_2^-/\text{Cl}^-$  molar ratio in concrete.

## Experiment

### 1. Materials

Diameter of 10mm, 80mm long light round steel bar, before immersed in a solution of water with acetone and sandpaper surface oil and passivation film were treated by using, the reinforcing steel bars are coated with epoxy resin at the interface of the solution and the bottom of the reinforcing bar. Nitrite solution with 35% concentrations of Calcium nitrite; Simulation of pore solution pure calcium hydroxide, potassium hydroxide, sodium hydroxide according to a certain proportion.

### 2. Methods

Simulated pore solution: Simulation of concrete pore solution by high pressure extraction of concrete pore solution analysis results, the simulated pore solution configuration results as shown in Table 1.

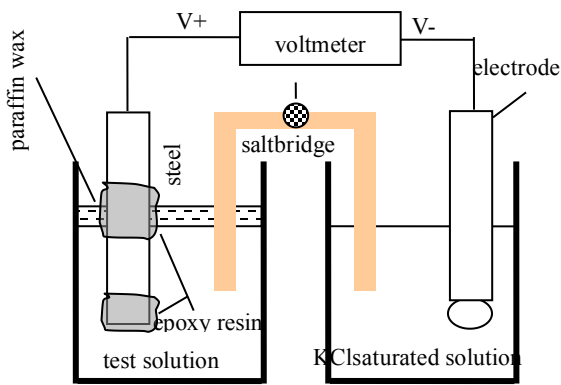
Saltbridge production: Add agar 35g, potassium chloride 350g and heat dissolved in 1L water in

the beaker. After completely dissolved, pour the solution into the siphon and adjust the length.

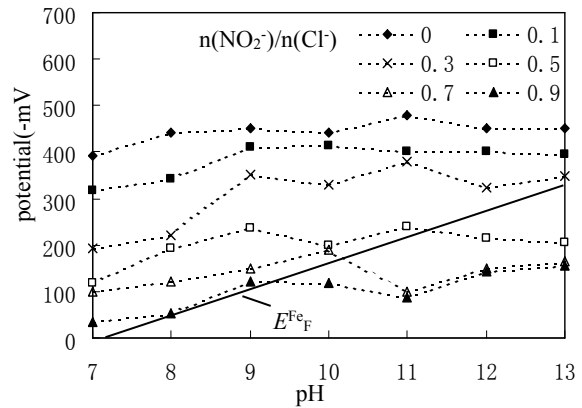
**Table 1** pH value, the concentration of  $\text{Cl}^-$  and  $\text{NO}_2^-$

Test solution	Index
PH value	7~13
$\text{Cl}^-$ concentration	1%
$n(\text{NO}_2^-)/n(\text{Cl}^-)$	0,0.1,0.3,0.5,0.7,0.9

Test model: The test model is shown in Fig.1. Steel, salt bridge and the reference electrode with a round cover fixed hole. Covered with a layer of liquid paraffin solution on the surface of steel into the test solution, in order to prevent the potential in the determination process of carbonization solution to change the pH value. Insert salt and silver chloride electrode at the other end of saturated potassium chloride solution (reference electrode). The natural potential of steel surface is measured with high input impedance voltage meter to 1 weeks, and the potential value tended to be stable.



**Fig.1.** Corrosion test model of steel bar



**Fig.2.** natural potential test in the test solution

## Results and discussion

### 1. Natural potential variation of steel

The natural electrode potential of the test steel immersed in the solution for seventh days as Fig.2. With the increase of the pH value the natural potential of the reinforcing bar is negatively moved when the  $\text{NO}_2^-/\text{Cl}^-$  molar ratio was the same; While the pH value is certain, the natural potential is moving forward with the increase of  $\text{NO}_2^-/\text{Cl}^-$  molar ratio.

### 2. Relationship between natural potential and molar ratio of reinforcement

When the solution is  $25^\circ\text{C}$ , a linear relationship between the reinforced following Fred potential  $E^{\text{Fe}_F}$  and pH value of the solution:  $E^{\text{Fe}_F} = 630 - 59\text{PH}(\text{VS.SHE}) = 432 - 59\text{PH}(\text{VS.Saturated and Ag/AgCl})$ . The greater the  $E^{\text{Fe}_F}$ , the greater the activity; the smaller the  $E^{\text{Fe}_F}$ , the greater the blunt<sup>[5]</sup>. So pH is small, the greater the potential Fred, not easy passivation, and vice versa. As shown in Fig.3, when  $\text{pH}=7$ , it has a approximate linear relationship between  $\text{NO}_2^-/\text{Cl}^-$  molar ratio  $M$  of each test solution and Fred potential and the measured potential difference  $E^{\text{Fe}_\Delta}$ , which under the molar ratio. The molar ratio of  $\text{NO}_2^-/\text{Cl}^-$  increases when the bar potential test solution is close to Fred potential,  $E^{\text{Fe}_\Delta} = 338 - 308M$  obtained by linear regression. So in  $\text{pH}=7$ , simulated pore solution potential at Fred potential of  $\text{NO}_2^-/\text{Cl}^-$  reinforced ratio  $M_F=1.1$ .

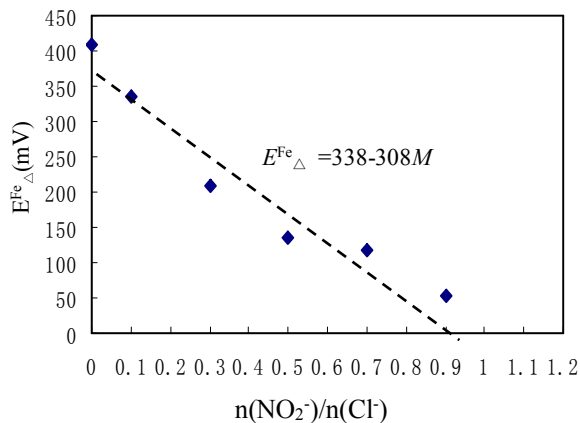


Fig.3.  $n(\text{NO}_2^-)/n(\text{Cl}^-)$  and increase potential

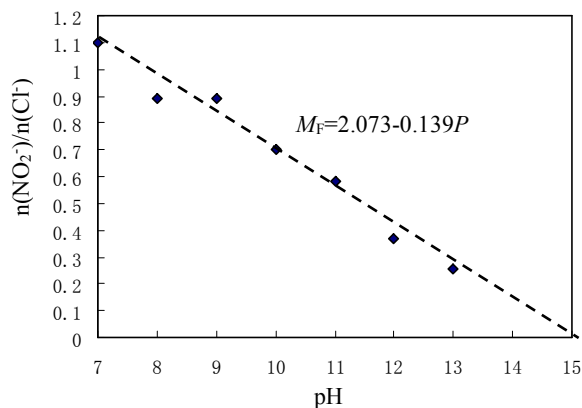


Fig.4. Effect of pH value on  $\text{NO}_2^-/\text{Cl}^-$  molar ratio

Similarly, test solution for  $\text{pH}=8 \sim 13$ , it has an approximate linear relationship between  $\text{NO}_2^-/\text{Cl}^-$  molar ratio  $M$  of each test solution and Fred potential and the measured potential difference  $E^{\text{Fe}}_{\Delta}$ , which is under the molar ratio. As shown in Fig.4, the measured potential is less than Fred potential and tends to be straight. The regression equation of the molar ratio of  $M_F$  which reached Fred potential and pH is  $M_F = 2.073 - 0.139\text{pH}$ . Therefore, chlorine salt simulated concrete pore solution, when the pH value is 12.6, the Fred potential required molar ratio of  $\text{NO}_2^-/\text{Cl}^-$  is only 0.32, which is less than the critical molar ratio of concrete. While the simulation concrete pore solution which has been carbonated, when the pH value is 8.3, the reinforced surface to Fred potential required  $\text{NO}_2^-/\text{Cl}^-$  molar ratio of 0.92. That concrete containing chloride salt also suffers from carbonization composite degradation, inhibition of corrosion of reinforcement required molar ratio of  $\text{NO}_2^-/\text{Cl}^-$  for not carbonation of concrete is about 3 times.

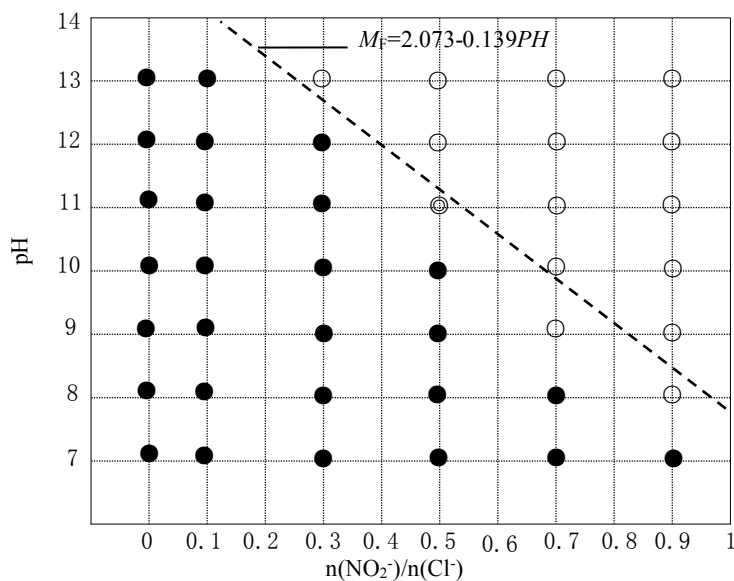


Fig.5. Corrosion of reinforcing steel bars

The reason for the value of  $\text{NO}_2^-/\text{Cl}^-$  for inhibiting the corrosion of steel bars in the simulated pore solution is less than that in the mortar hole solution: In the mortar, the steel bar surface is always in a state of unevenness, so the steel surface is easy to produce the macro cell corrosion caused

by the defect of the cell and the structure. While the steel surface in the water solution is in a homogeneous and continuous liquid phase, so the low concentration of nitrite is enough to inhibit the corrosion of the steel bar<sup>[6]</sup>.

### 3. Observation results

In Fig.5, the corrosion of reinforcing steel in the simulated pore solution is observed by the naked eye. Among them, ○ representative does not corrode, ⊙ representative uncertain, and ● representative corrosion.

Can be seen from the figure, When the  $\text{NO}_2^-/\text{Cl}^-$  molar ratio is less than 0.1, the pH value in the range of 7 ~ 13 steel surface are different degrees of corrosion, and the pH value is equal to 7, even if the  $\text{NO}_2^-/\text{Cl}^-$  molar ratio of 0.9 also appeared corrosion. The regression line between the molar ratio and pH, the lower part is the corrosion area, and the upper part is the non corroded area, the corrosion condition of the steel surface is basically consistent with the actual corrosion condition. When the chloride content of a certain, the linear regression equation between  $\text{NO}_2^-/\text{Cl}^-$  molar ratio of steel surface reached Fred potential and pH value is reasonable.

### Conclusion

(1) When the pH value is certain, the natural electrode potential of the reinforced bar tends to move forward with the increase of  $\text{NO}_2^-/\text{Cl}^-$  molar ratio, which is beneficial to the inhibition of the corrosion of the steel. When the  $\text{NO}_2^-/\text{Cl}^-$  molar ratio is constant, the pH value increases, and the natural electrode potential tends to move toward the negative direction. But fluoride Ryder potential with pH increase also tends to negative direction. Therefore, when the pH value was high while the potential was low, it can also protect the passivation film from being corroded.

(2) The  $\text{NO}_2^-/\text{Cl}^-$  molar ratio of molar ratio less than the critical  $\text{NO}_2^-/\text{Cl}^-$  molar ratio of the actual concrete is suppressed in the concrete simulated pore solution. This may be because the surface of the reinforcing steel in the concrete is not in a state of uniform with respect to the water solution, generating a macro cell easily.

(3) There is a linear relationship between the  $\text{NO}_2^-/\text{Cl}^-$  mole ratio and the pH value of the solution in the simulation of concrete in the solution of the simulated pore solution  $M_F=2.073-0.139\text{pH}$ , when the pH value of the simulated common concrete pore solution is 12.6, the molar ratio of corrosion inhibition is 0.32; While the pH value of the pore solution of carbonated concrete is 8.3, the ratio of  $\text{NO}_2^-/\text{Cl}^-$  to mole ratio is 0.92, which is about 3 times of that of ordinary concrete.

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