INTERFACE CHARACTERISTICS OF STEEL AND CONCRETE
IN PRESENCE OF CHLORIDE AND CARBONATION

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This paper aimed to present the morphology features and elements' distribution at the interface between steel and concrete in the presence of chloride and carbonation by means of electron probe (EPMA) and X-ray energy spectrum analysis (EDX-SEM). The results showed that the corrosion products of steel bars at the interface of steel and cement paste in chlorinated reinforced concrete diffusing into concrete through the steel-concrete interface. According to the penetration depth of corrosion products, the corrosion degree of the steel bars in the concrete can be determined. The chloride ions produced by the decomposition of Friedel salt in the cement paste migrated to the surface of steel bar in non-carbonated zone. As a result, the concentration of chloride ions accumulated on the surface of steel bars reached the critical concentration of corrosion, which increased the probability of steel corrosion. When concrete was mixed with nitrite, NO2-AFm, which was evenly distributed originally in the cement paste, decomposed into nitrite ions under carbonation and diffuses to non-carbonized zone. This increased the NO_2^-/Cl^- molar ratio around the steel bar and effectively prevented corrosion of steel bars.

Keywords: steel-concrete interface, carbonation, chloride salt, EPMA, elements distribution

1. Introduction

A large number of examples of reinforced concrete structure failure show that the main causes of steel corrosion are chlorine salt and carbonation. Most concrete structures are in service under the dual action of carbon dioxide and chlorine ion [1-3]. At present, the researches on the corrosion mechanism of reinforced concrete under the action of carbonation and chloride corrosion are mainly concentrated on the concrete pore solutions [4-6]. Scholars propose different critical value of chlorine ion concentration. This is partly because the environmental complexity of different pH, temperature, humidity and chloride concentration [7, 8]. And partly results of various factors affecting passive film damage, including the surface state, alloy and iron composition of the steel, as well as the permeability of concrete [9-12]. The characteristics of the passivation film with thickness, composition and stability are affected by the polarization potential, polarization time and ion concentration. The corrosion of steel reinforcement is attributed to the change of passivation film composition and structure. The microstructure features of passivation film are related to passivation potential and time [13, 14]. The change of concrete composition and structure also affect the integrity of passivation film. During the carbonation process in chloride containing concrete, chloride ions generated by the decomposition of Friedel compound salt migrate

and concentrate to the surface of steel reinforcement, which significantly reduces the initial corrosion value of chloride. Thus, the corrosion probability of the carbonation front is increased, and the corrosion rate is accelerated [15, 16]. Therefore, to clarify the failure process of passivation film and structure change in presence of carbonation and chloride corrosion is an important content that needs to be solved urgently, so as to improve the environment of steel bar in concrete.

This paper aimed to present the elements' distribution at the interface between steel and concrete in the presence of chloride and carbonation by means of electron probe (EPMA) and X-ray energy spectrum analysis (EDX-SEM), so as to clarify the influence of carbonation and chlorine on the corrosion failure mechanism of steel reinforcement. This provided a theoretical basis for improving the service life of reinforced concrete structures.

2. Experimental
2.1 Sample preparation

The HPB300 round steel reinforcement bars with 8mm diameter and 180mm length were removed with 10% ammonium citrate solution. After the oxide on the surface was dissolved, the steel bar was rinsed by deionized water and dried with a dry towel. Both ends of the steel bars were polished with a sandpaper of 400, 500 and 800 grit sandpaper to be bright mirror, and then wiped off

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with 95% acetone. Ordinary Portland cement P•O42.5 with water-cement ratio of 0.32 was used. The mixing amount of sodium chloride was 0.5% of the mass of cement. The amount of NaNO$_3$ satisfied $n(NO_2^-)/n(Cl^-)=1.2$. The specimen was a cylinder with diameter of 36mm and height of 160mm. As shown in Figure 1, the thickness of the protective layer was 14mm. Both ends of steel bars were exposed 10mm and sealed with epoxy adhesive.
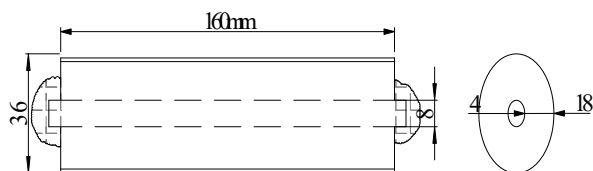
Fig. 1-Specimen diagram.

The specimens were demoded after curing for 1day and wrapped with plastic film to be cured for 28 days. Then, specimens were put into the thermo-wet box for dry and wet circulation for 30 times to accelerate the corrosion of steel reinforcement, as shown in Figure 2.
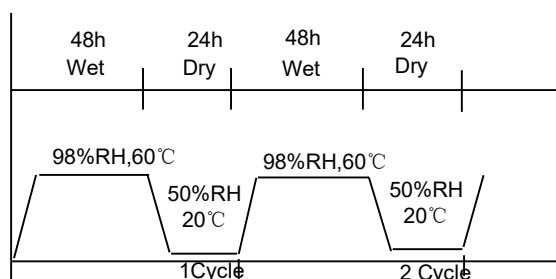

Fig.2-Cycles of wetting and drying.

2.2 Testing procedures
Carbonation depth measurement

Net cement slurry specimens cured for 28 days were sealed for cross sections with epoxy resin and the sides of cylinder were left to be accelerating surface. The parameters of the carbonation box were set as 20% CO$_2$ concentration and 60% relative humidity. The samples were taken out and cut every 7 days. The tested surface was cleaned by bellow and sprayed by 1% phenolphthalein alcohol solution. The depth of uncolored cement stone was measured by vernier caliper, so as to determine the carbonation depth [17-19].

Electron probe test

The carbonized cylinder specimen was sawn with a hacksaw in a direction parallel to the circular section. For the section to be scanned with electron microprobe, smoothed it with a fine particle sandpaper and scraper, then gently cleaned it with a fine brush, and blew off the small particles adhering to the surface of the sample with a hair dryer. Finally it was washed and dried the section for later use with anhydrous alcohol. The surface of the sample was conductive treated by SBC-12 ion sputtering instrument (China science & technology co., LTD.), and analyzed by electron probe after being sputtered a 20nm thick gold-plated film.

Electron probe was EPMA-1600 produced by shimadzu co., LTD. The acceleration voltage was 0~30kV and the magnification is 20~3×10^5. The elemental analysis range is 5B-92U, and the X-ray extraction angle is 52.5°.The main accessory was the spectrometer (WDS), which can be used for the analysis of new, complex, micro and fine minerals in solid materials such as materials science, geology and microelectronics. In this paper, surface scanning of cement slurry specimens and line-scanning component analysis of the central dot were mainly carried out. The acceleration voltage was 15kV and the beam current was 10nA [20, 21].
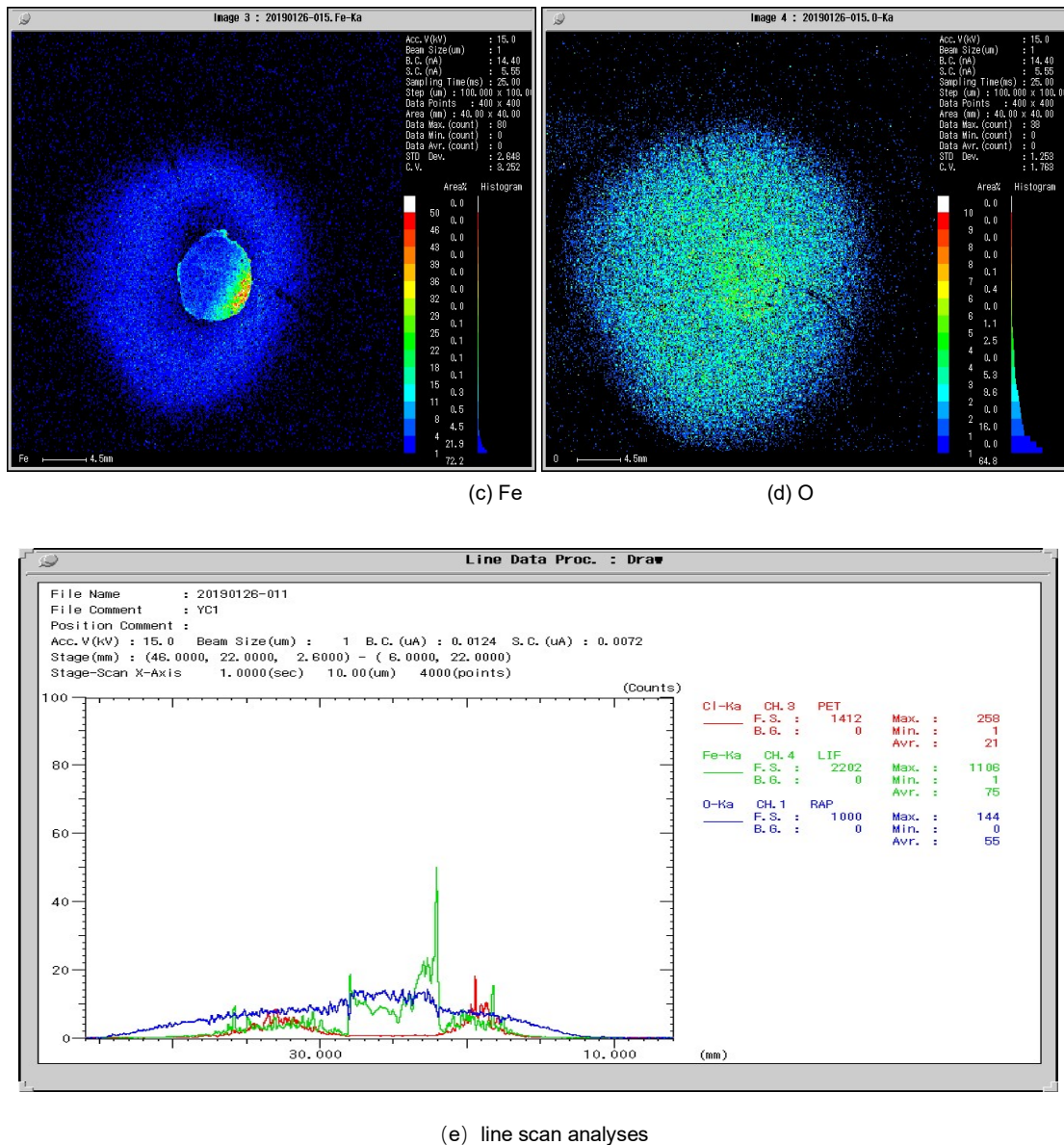

(a)Top view of cement paste   (b) Cl

(c) Fe   (d) O

(e) line scan analyses
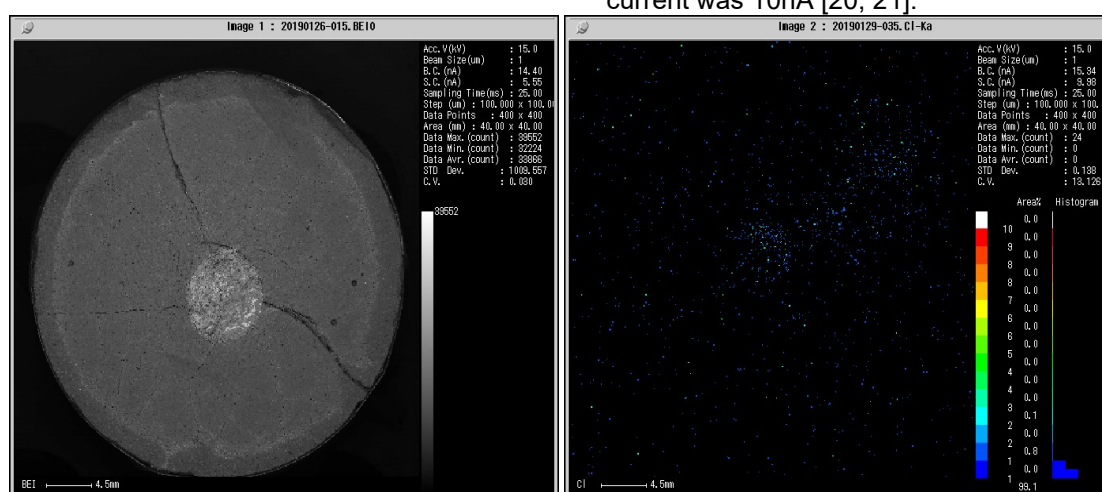
Fig.3-Elements distribution of steel bar and cement paste interface with chloride salt of 0.5%

X ray energy spectrum analysis

S4800 cold-field emission scanning electron microscope (SEM) was used to observe the morphology of corrosion products on the surface of steel reinforcement, and the elemental composition was analyzed by combining energy disperse spectroscopy (EDS) [22].

3. Results and Discussion

3.1 Interface characteristics of reinforcement-cement slurry under chloride corrosion

Figure 3 shows the surface scan and line scan through the central point in the interface of reinforcement-cement slurry with chloride of 0.5%. It is visible that chlorine ions are evenly distributed in the interface of cement slurry and oxygen is sufficient around the steel bar. After 30 dry and wet cycles, the cement samples with steel bars corrode seriously, and the corroded products diffuse through the reinforcement - cement slurry interface to a certain depth inside the cement slurry. It is drawn from energy spectrum analysis of corrosion substances on the surface of steel bars in chlorine-containing cement that the main elements are iron, oxygen, calcium, silicon, sodium, aluminum, potassium, carbon, etc. The elements content are shown in Table 1. The corrosion products are fully integrated with cement hydration products, as shown in Figure 4.

3.2 Interface characteristics of reinforcement-cement slurry under the combined action of carbonation and chlorine salt

Fig.5 shows the interface characteristics of reinforcement-cement slurry containing 0.5% chloride after 30 dry and wet cycles under carbonation. It is observed that the content of oxygen around the reinforcement is adequate. Before carbonation, chlorine ions are evenly distributed in the cement slurry. After carbonation,

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Table 1

Elements content with specimen of 0.5% chloride salt

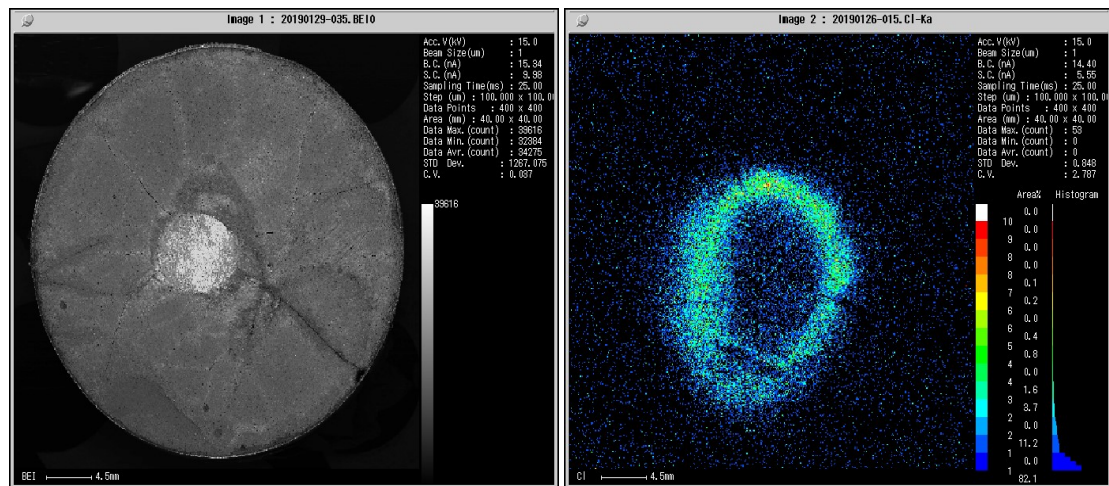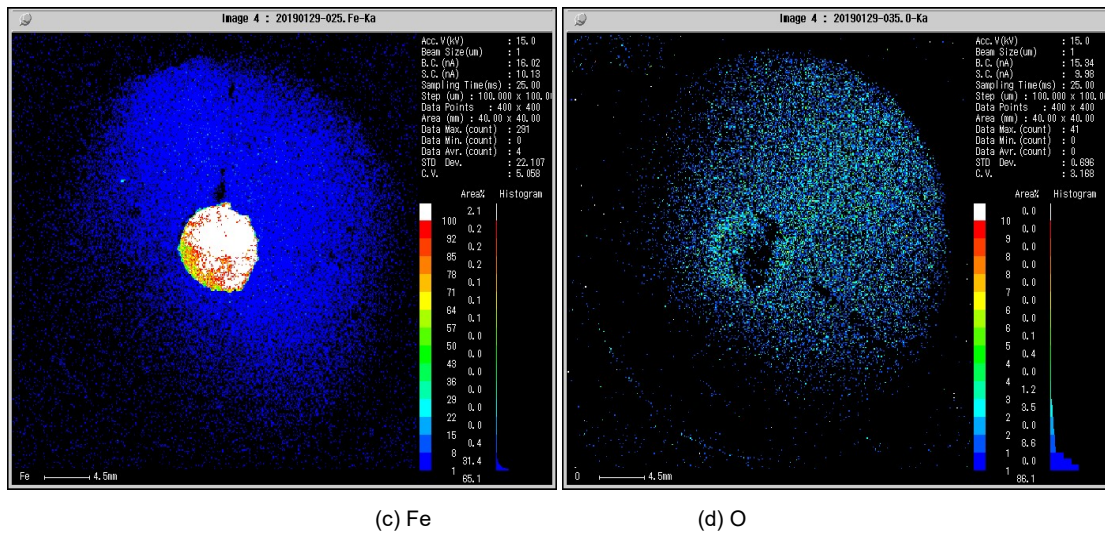| Element	unn. C/wt.%	norm. C/wt.%	Atom. C/at.%	Compound	Comp. C
Oxygen	23.80	25.40	51.41	FeO	0.00
Iron	56.52	60.32	34.98		57.61
Silicon	2.93	3.13	3.60	SiO_2	6.69
Calcium	8.20	8.75	7.07	CaO	12.24
Potassium	0.51	0.55	0.45	K_2O	0.66
Sodium	1.20	1.28	1.80	Na_2O	1.72
Aluminium	0.54	0.58	0.68	Al_2O_3	1.09
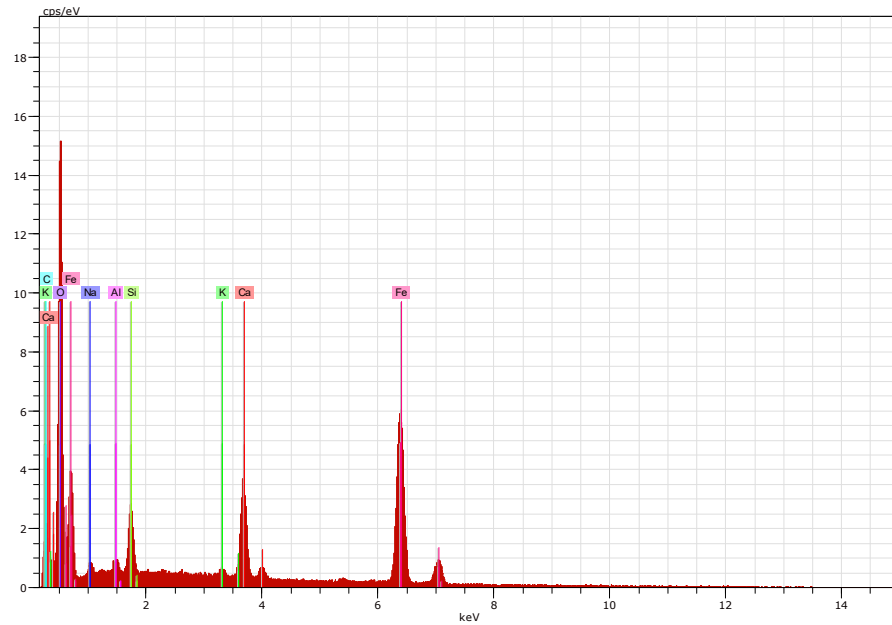
Fig.4- SEM-EDX of corrosion products on the steel surface.
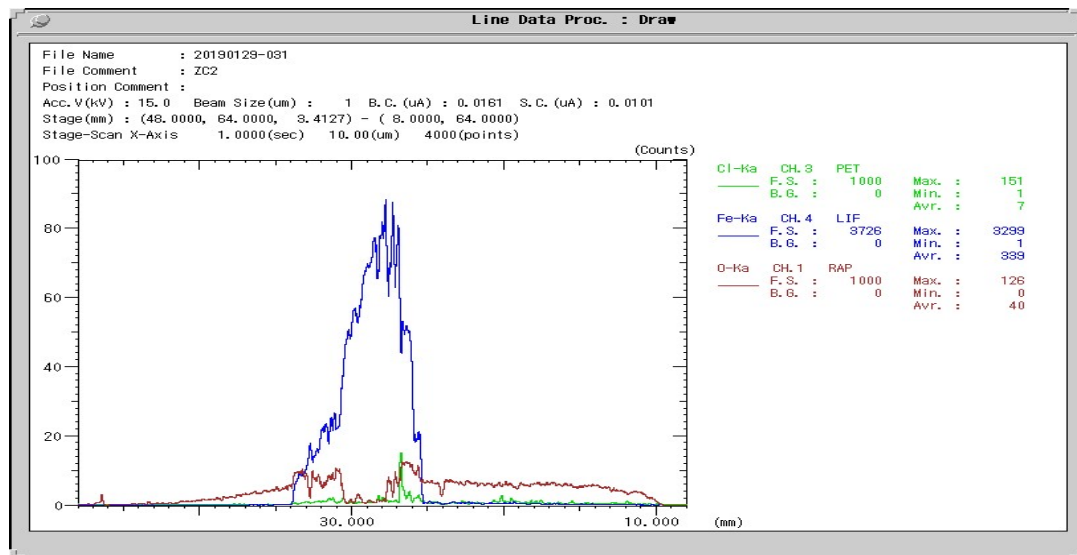

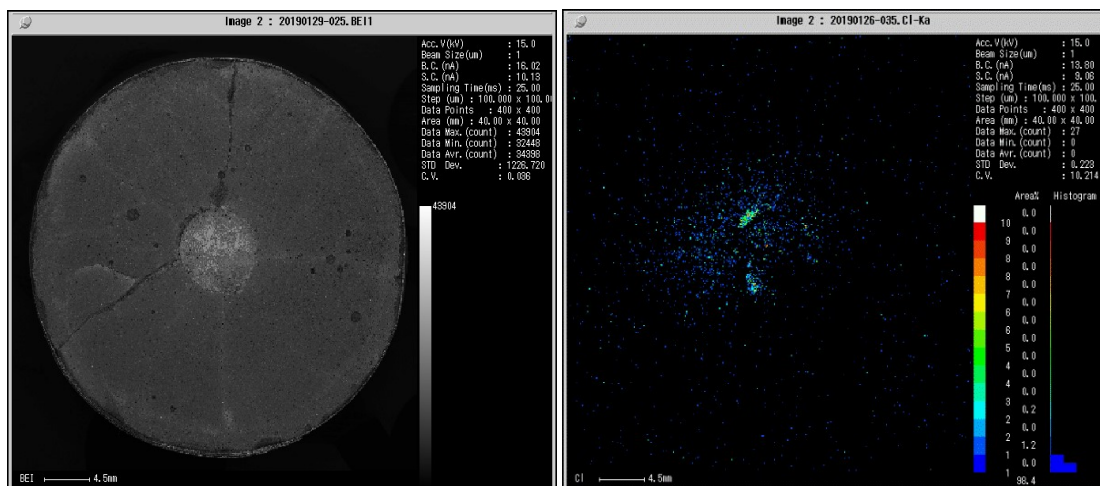(a)Top view of cement paste　　　　　　　　　　(b) Cl

(c) Fe   (d) O

(e) line scan analyses

Fig.5-Elements distribution of steel bar and cement paste interface under carbonation and chloride salt.

chlorine ions migrate and concentrate, leading to the reduction of the initial chlorine ion concentration causing the corrosion of steel reinforcement. The chloride ion migration and microstructure change during the carbonation of cement slurry have an important influence on the corrosion performance of steel reinforcement. The chloride ions in concrete are divided into solidified chloride ions and free chloride ions. Only free chloride ions can lead to the corrosion of steel reinforcement bars. Before carbonation, the distribution of chlorine ions in the concrete is uniform, and the total chlorine ion concentration is the sum of the solidified chlorine ion concentration and free chlorine ion concentration. With the progress of carbonation, new free chlorine ions are generated by the decomposition of Friedel complex salt in the carbonation zone, which increased the concentration of free chlorine ions. Under the action of concentration diffusion, free chlorine ions will inevitably diffuse and migrate to the non-carbonized area on the surface of the internal steel bar, resulting in the increase of the concentration of free chlorine ions in the non-carbonized area. That is, the chloride ion concentration on the surface of steel reinforcement is the sum of the initial solidified chloride ion concentration, the initial free chloride ion concentration, and the free chloride ion migrating from carbonation zone, which is the internal reason for the increase of the total chloride ion concentration in EPMA analysis. In other words, the free chlorine ion accumulates in the non-carbonized area of the steel bar surface after carbonation, which aggravates the corrosion probability of the steel bar in this area. From the above ion migration theory, it can be drawn that a more stringent maximum allowable content of chlorine ion under the combined action of carbonation and chlorine salt should be formulated [23, 24].
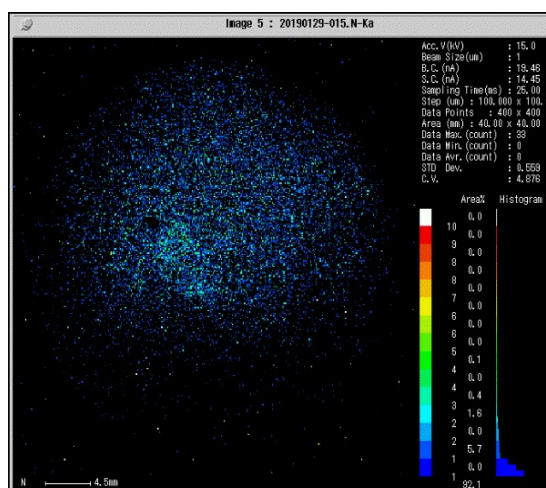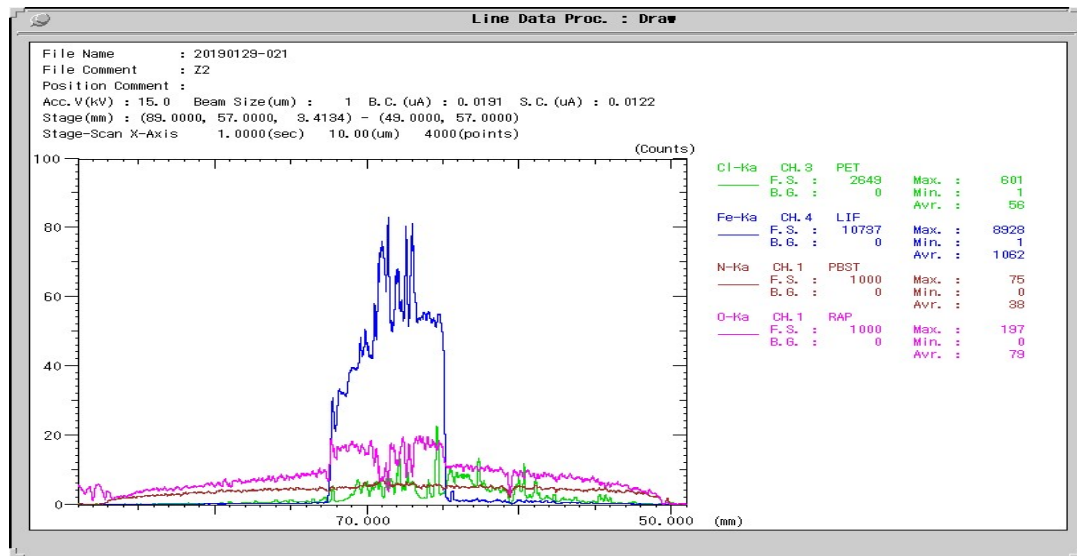
(a)Top view of cement paste

(b) Cl
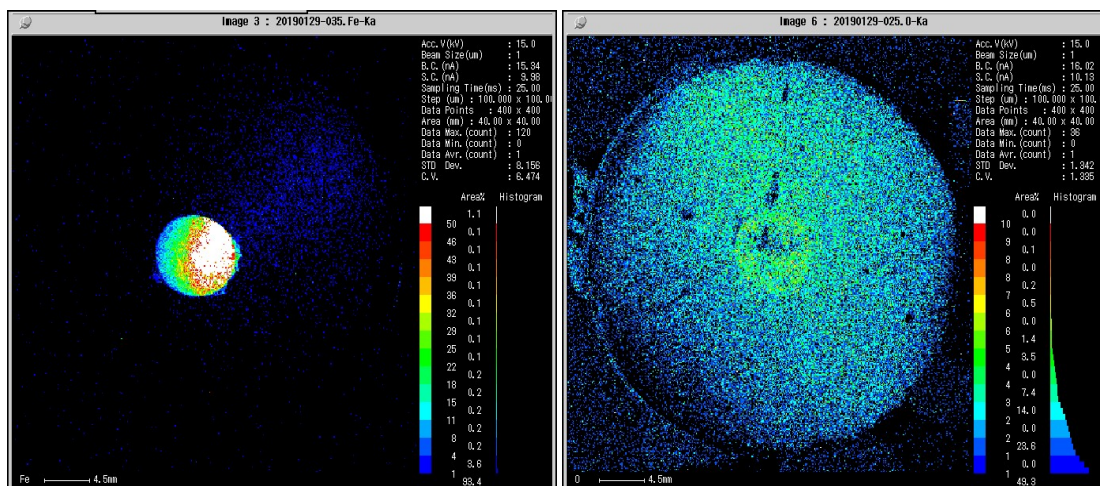
(c) Fe

(d) O

（e） N

(f) line scan analyses

Fig.6-Elements distribution of steel bar and cement paste interface containing nitrite salt.
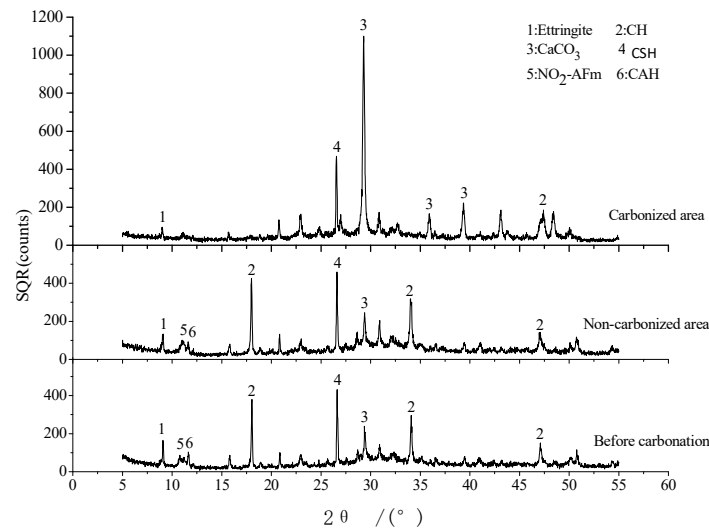

Fig.7-XRD patterns of cement paste containing nitrite

3.3 Interface characteristics of reinforcement-cement slurry under the action of nitrite rust inhibition

Fig.6 shows the interface characteristics of reinforcement-cement slurry containing 0.5% chloride after 30 dry and wet cycles under carbonation. It's shown that the content of oxygen around the reinforcement is adequate. Chloride ion distributes evenly in the interface of net cement slurry before carbonation. The chloride ion migration and concentration make the chloride ion concentration on the surface of the steel bar reach a higher level in the chlorine-containing concrete without nitrite after carbonation, as shown in Figure 5(b). After hydration of the cement slurry containing nitrite, a new crystalline phase NO_2-AFm of hydration product is generated and evenly

distributed in the cement slurry, as shown in Fig.7. During the carbonation process, NO_2-AFm decomposes to form nitrite ions and diffuses to the non-carbonized zone, resulting in the decrease of NO_2^- content in the carbonized zone and the increase in the non-carbonized zone. As shown in Fig.6 (e), the content of NO_2^- on the surface of the reinforcement also increases. The steel bar can be effectively protected when the nitrite content is enough to make the mole ratio of NO_2^-/Cl^- around the steel bar in concrete reach the critical value of rust resistance [25-27]. By comparing fig. 6(b) with Fig. 5 (b), it can be seen that the distribution of chloride ions on the surface of the reinforcement bar is significantly reduced under the action of nitrite, which is a good proof of this phenomenon. As can be seen from the distribution diagram of

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elements at the rebar - slurry interface of the nitrite specimen under the combined action of carbonation and chlorine salt in fig. 6(c), the iron element diffusion is not obvious in the cement slurry around the reinforcement, indicating that the passivation film on the surface of the reinforcement is relatively intact.

4. Conclusions

Corrosion products at the interface between reinforcement and cement slurry in concrete containing chlorine are diffused into cement slurry through the interface. According to the degree of iron penetration in cement slurry, the corrosion degree of steel reinforcement in cement slurry can be judged.

Under the carbonation, the chloride ions generated by the decomposition of Friedel compound salt in the chlorinated concrete migrated to the non-carbonized zone, resulting in the small initial chlorine ion content on the surface of the steel bar to reach the critical concentration value.

When the cement slurry containing nitrite is carbonized, the NO_2-AFm evenly distributed in the cement slurry is decomposed into nitrite ions and diffused to the non-carbonized area. Thus, the content of NO_2^- reduces in the carbonized area and increases in the non-carbonized area, which improves the mole ratio of NO_2^-/ Cl^- on the surface of steel reinforcement and effectively prevents the corrosion of steel reinforcement.

REFERENCES

[1] F. Marquesp, C. Chastre, N. Ângel, Carbonation service life modelling of RC structures for concrete with Portland and blended cements, Cement and Concrete Composites, 2013, **37**(3),171.
[2] J. Z. Liu, M. F. Ba, Y. G. Du, Effects of chloride ions on carbonation rate of hardened cement paste by X-ray CT technic, Construction and Building Materials, 2016, **122**(7),619.
[3] J. Williamson, O. B. Isgor, The effect of simulated concrete pore solution composition and chlorides on the electronic properties of passive films on carbon steel rebar, Corrosion Science, 2016,**106**: 82.
[4] J. J. Shi, W. Sun, G. Q. Geng, Influence of simulated concrete pore solution on reinforcing steel passivation, Journal of Building Materials, 2011, **14**(4), 452.
[5] J. Z. Liu, W. J. Yuan, Z. M. He, Microstructural characteristics of hardened cement against combined effect of carbonation and chloride salt, Acta Materiae Compositae Sinica, 2015, **32**(5), 1536.
[6] Z. Y. Ai, J. Y. Jiang, W. Sun, Passive behaviour of alloy corrosion-resistant steel Cr10Mo1 in simulating concrete pore solutions with different pH, Applied Surface Science, 2016, **389**, 1126.
[7] R. Liu, L. H. Jiang, J. X. Xu, Influence of carbonation on chloride-induced reinforcement corrosion in simulated concrete pore solutions, Construction and Building Materials, 2014, **56**, 16.
[8] V. S. Tatyana, K. L. veronika, A. T. Galina, The effect of microstructure and non-metallic inclusions on corrosion behavior of low carbon steel in chloride containing solutions, Corrosion Science, 2014, **80**, 299.
[9] Q. X. Li, Z. Y. Wang, W. Han, Characterization of the rust formed on weathering steel exposed to Qinghai salt lake atmosphere, Corrosion Science, 2008, **50**, 365.
[10] K. Arto, H. Mari, L. Jukka, Corrosion products of carbonation induced corrosion in existing reinforced concrete facades, Cement and Concrete Research, 2015, **78**, 200.
[11] H. B. Gunay, P. Ghods, O. B. Isgor, Characterization of atomic structure of oxide films on carbon steel in simulated concrete pore solutions using EELS, Applied Surface Science, 2013, **274**, 195.
[12] A. S. Yaro, K. R. Abdul-Khalik, A. A. Khadom, Effect of CO_2 corrosion behavior of mild steel in oilfield produced water, Journal of Loss Prevention in the Process Industries, 2015, **38**, 24.
[13] H. Bruno, L. Valerie, M. Frederic, Electrochemical behavior of mild steel in concrete: Influence of pH and carbonate content of concrete pore solution, Electrochimica Acta, 2005, **51**, 172.
[14] Y. Wang, S. Nanukuttan, Y. Bai, Influence of combined carbonation and chloride ingress regimes on rate of ingress and redistribution of chlorides in concretes, Construction and Building Materials, 2017, **140**, 173.
[15] S. Poyet, W. Dridi, V. L'Hostis, Microstructure and diffusion coefficient of an old corrosion product layer and impact on steel rebar corrosion in carbonated concrete, Corrosion Science, 2017, **125**, 48.
[16] P. Ghods, O. B. Isgor, F. Bensebaa, Angle-resolved XPS study of carbon steel passivity and chloride-induced depassivation in simulated concrete pore solution, Corrosion Science, 2012, **58**, 159.
[17] P. Ghods, O. B. Isgor, J. R. Brown, XPS depth profiling study on the passive oxide film of carbon steel in saturated calcium hydroxide solution and the effect of chloride on the film properties, Applied Surface Science, 2011, **257**, 4669.
[18] Q. Wang, D. Q. Wang, H. H. Chen. The role of fly ash microsphere in the microstructure and macroscopic properties of high-strength concrete, Cement and Concrete Composites, 2017, **83**, 125.
[19] J. Z. Liu, J. S. Shen, J. L. Yan, Microstructural characteristics of steel corrosion products under carbonation and chloride salt, Acta Materiae Compositae Sinica, 2018, **35**(9), 2587.
[20] Q. F. Li, Y. Ge, W. C. Yang, Effect of sodium sulfate and sodium nitrite on air-void system in air-entrained concrete, Magazine of Concrete Research，2016, **68**, 1200.
[21] I. Fayala, L. Dhouibi, X. R. Novoa, Effect of inhibitors on the corrosion of galvanized steel and on mortar properties, Cement and Concrete Composites, 2013, **35**, 181.
[22] C. M. Goulart, A. E. Souza, C. A. Martine, Experimental and theoretical evaluation of semicarbazones and thiosemicarbazones as organic corrosion inhibitors, Corrosion Science, 2013, **67**, 281.
[23] E. Rakanta, T. Zafeiropoulou, G. Batis, Corrosion protection of steel with DMEA-based organic inhibitor, Construction and Building Materials, 2013, **44**, 507.
[24] H. Verbruggen, H. Terryn, I. Graeve, Inhibitor evaluation in different simulated concrete pore solution for the protection of steel rebar, Construction and Building Materials, 2016, **124**, 887.
[25] L. Yohai, W. Schreiner, M. B. Valcarce, Inhibiting steel corrosion in simulated concrete with low phosphate to chloride ratios, Journal of the Electrochemical Society, 2016, **163**, 729.
[26] X. Z. Li, J. Z. Liu, Y. H. Dai, Effect of carbonation on nitrite ion distribution in cement paste, Journal of Jilin University: Technology Edition, 2019, **49**(4),1162.
[27] Y. H. Cao, S. G. Dong, D. J. Zheng, Multifunctional inhibition based on layered double hydroxides to comprehensively control corrosion of carbon steel in concrete, Corrosion Science, 2017, **126**(9),166.

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