

Efficiency of electrochemical chloride removal from concrete at different environmental temperatures

S. Jin, J. Xia and W-L. Jin
Zhejiang University, Hangzhou, China

Z-Y. Yu and J-Y. Hu
Zhejiang Electric Power Corporation Research Institute, Hangzhou, China

Q. Lyu
Southeast University, Nanjing, China

X. Zhong
Yangzhou University, Yangzhou, China

ABSTRACT

Electrochemical chloride removal (ECR) is an effective and curative method to treat existed reinforced concrete structures about to suffer or already suffering from chloride attack, however, its application is still limited due to its side effect and efficiency, including the velocity and maximum capacity of chloride removal. This paper presents a temperature related numerical transport model to study the effect of temperature on efficiency of electrochemical chloride removal from concrete. Based on Fick's law and Nernst-Planck equation with Gauss' Law, temperature effect, chloride binding, multi-species coupling, electrochemical reactions were taken into account in this model. Temperature effect was considered on diffusion coefficient, chloride binding, ions migration capacity as well as electrolyte concentration. The model was validated by the comparison between the calculated results and experimental data. The results indicate that temperature dose have a considerable influence on electrochemical chloride removal and controlling temperature during treatment is a practical method to improve the electrochemical chloride removal when applied current density is not amplified.

Keywords: ECR; numerical model; temperature; diffusion coefficient; binding; migration

1.0 INTRODUCTION

Chloride attack is a common cause of deterioration of the reinforced concrete structures exposed to sea-water or de-icing salt (Jin and Zhao, 2014). Once the chloride concentration at the reinforcing bar reaches the threshold, the passive layer would be destroyed, leading to the corrosion of the steel rebar. Electrochemical chloride removal (ECR) is an effective and curative method to treat existed reinforced concrete structures about to suffer or already suffering from chloride attack (Yodsudjai and Saelim, 2014). A direct current is applied between the external anode and the cathodically polarized reinforcing steel. The harmful chloride ions are extracted to the anode by the electric potential gradient and the alkalinity at the rebars increases due to the hydroxyl produced by the electrode reaction at the cathode, which helps the regeneration of the passive layer (see Fig. 1) (Elsener and Angst, 2007).

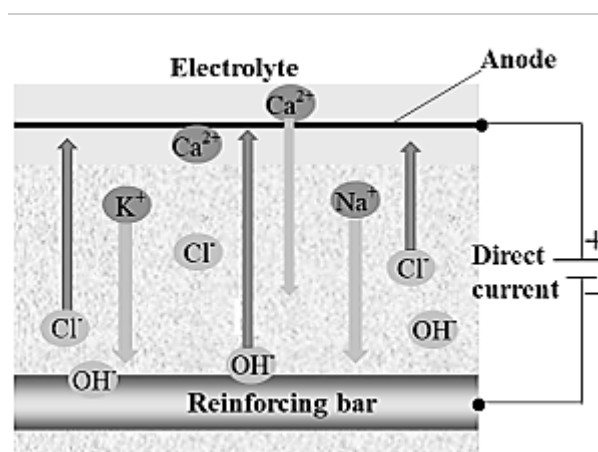


Fig. 1. Mechanism of ECR Treatment

However, the application of ECR technique is still limited due to its side effect and efficiency, including the velocity and maximum capacity of chloride removal. Therefore, an efficient and economical

method to improve the efficiency without more side effect is very significant.

Though the current density, treatment duration (Guo and Gong, 2011), type of electrolyte (Jiang, 2008), distribution of reinforcing bars (Chang *et al.*, 2014; Garces *et al.*, 2006; Němeček *et al.*, 2018) and some other factors have been studied by many scholars, rare research could be found about the temperature influence on the ECR efficiency.

Banfill and Andrade had pointed out that the electric migration is the main mechanism during the ECR process (Andrade *et al.*, 1995; Banfill, 1997) and several studies have been conducted about the influence of temperature on the binding effect (Hussain and Rasheeduzzafar, 1993; Maslehuiddin *et al.*, 1997; Song *et al.*, 2007), diffusion coefficient (Dhir *et al.*, 1993; Saetta *et al.*, 1993; Tang, 1996) and migration flux which play important roles in the electric migration. Therefore, it seems meaningful to study the relationship of the temperature with the ECR efficiency.

This paper is aimed to study the influence of temperature on ECR treatment and to find an effective and harmless method to improve the ECR efficiency. Several concrete specimens were treated with ECR at the different temperatures and the numerical simulations of ECR process were performed.

2.1 Preparation of Concrete Specimens

Fifteen concrete specimens in the size of 150 × 150 × 300 mm were casted with two steel bars 20 mm in diameter located 50 mm away from the surface (see Fig. 2). The concrete mix design was given in Table 1. All specimens were cured in a curing chamber with the temperature of 20 ± 2°C and the relative humidity of 95% for 28 days.

Five surfaces of each concrete specimen were covered with ethoxyline resin except the treated one before the ECR treatment.

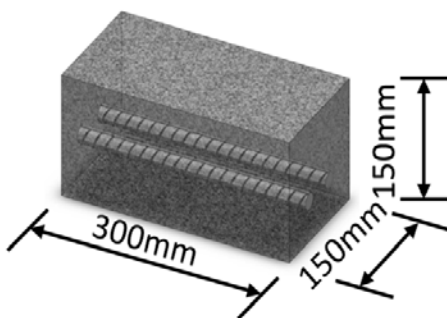


Fig. 2. Schematic of the Concrete Specimen

Table 1. Mix Design of Concrete Specimens

Water (kg/m ³)	Cement (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate (kg/m ³)	NaCl (relative to cement mass)	Super-plasticizer (relative to cement mass)
220	509	562	1044	3 %	1.6

2.0 EXPERIMENT

2.2 Electrochemical Chloride Removal System

The fifteen concrete specimens were divided into five groups and the specimens in Group A to D were treated with ECR process for 15 days at the temperatures of -10 °C, 0 °C, 20 °C and 50 °C respectively while the Group E was set as control group (see Table 2).

As shown in Fig. 3 for each specimen, a temperature sensor was put into the concrete through the hole drilled on the opposite of the treated surface and the other two sensors were placed in the electrolyte and the air respectively. The treated concrete surface was covered with a stainless-steel mesh and immersed in the saturated calcium hydroxide electrolyte. A constant voltage of 24 V was applied for 15 days during the ECR process. The whole system was placed into the temperature-controlled cabinets set as -10 °C, 0 °C, 20 °C, 50 °C respectively.

A percussion drilling was used to collect the concrete powder at the different depths in three regions. The domain at an outside distance 25mm of the rebar was designated as Region 1 while the domain right above the rebar as Region 2 and the domain between two rebars as Region 3 (see Fig. 4). The concentration of water-soluble chloride was measured using ASTM C1218/C1218M-99 (ASTM, 2015).

2.3 Results and Discussions

In each group, the mean values of the remained chloride concentrations at the 8 × 5 points could be calculated and the contour maps were plotted. It should be noticed that in Group A, the electrolyte froze and the electric current was almost 0, meaning that the ECR treatment had very limited effect at such a low temperature. The chloride concentrations measured in Group E were used to calculate the initial concentration and only three contour maps were drawn as Fig. 5.

The remained chloride concentrations were significantly different at the three temperatures, indicating that the temperature did have a nonnegligible influence during the ECR treatment. The average chloride concentration in group E,

which represented the initial chloride concentration was 77.4 mol/m^3 while the remained concentrations in concrete after the ECR treatment at 0°C were between $42 \sim 79 \text{ mol/m}^3$. The concentrations decreased to $12 \sim 48 \text{ mol/m}^3$ when the temperature was 20°C and at 50°C , the remained chloride concentrations were only $5 \sim 33 \text{ mol/m}^3$. It should be noticed that the difference of remained chloride concentrations between 0°C and 20°C was much larger than that between 20°C and 50°C , which implied that the impact of temperature on ECR efficiency might decrease when temperature increased.

Table 2. Treatment of Concrete Specimens for Each Group

Group	Treatment	Temperature
A		-10°C
B	ECR for 15 days at the temperatures of	0°C
C		20°C
D		50°C
E	Control group	

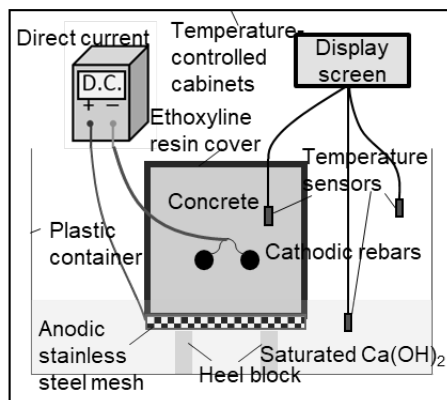


Fig. 3. Schematic of the ECR System

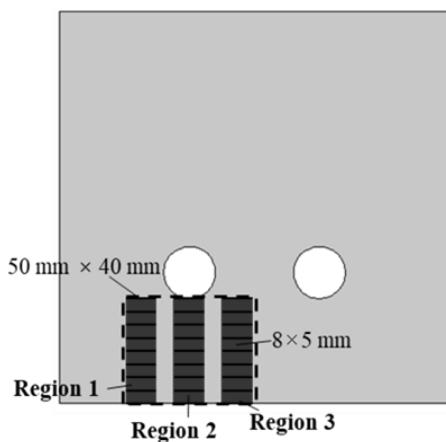


Fig. 4. Sampling Methods for Chloride Content Determination

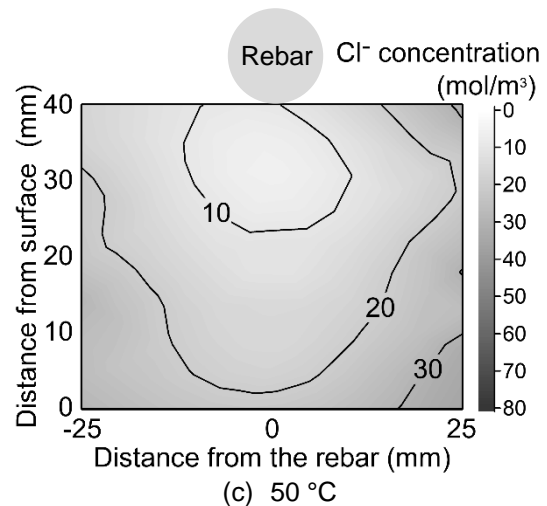
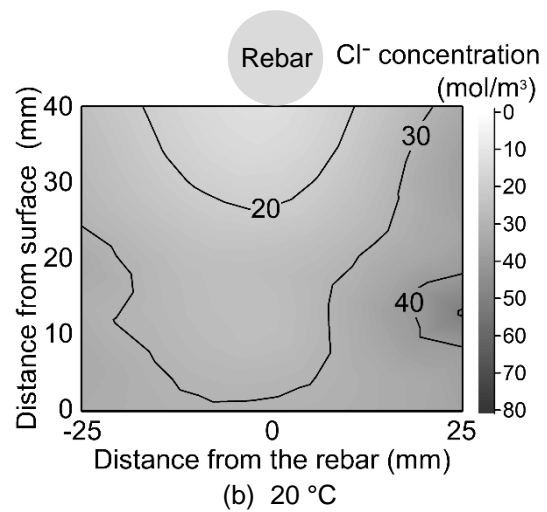
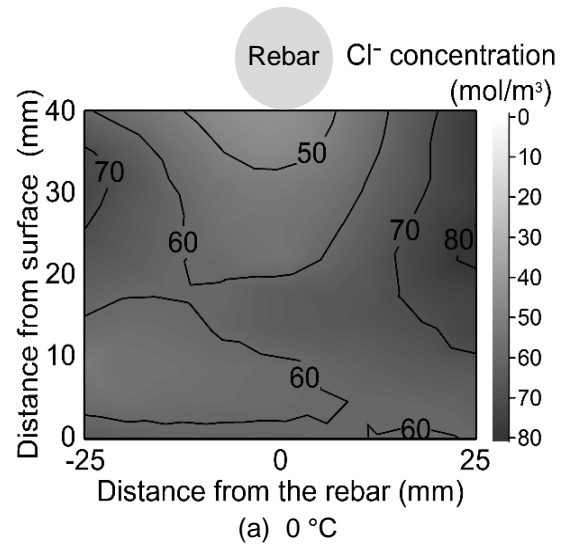


Fig. 5. Chloride distributions for various temperatures after ECR experiment

3.0 NUMERICAL MODEL

3.1 Model Establishing

As shown in Fig. 6, a 2-D square geometry representing the concrete in the size of $150 \times$

150 mm with two circle 20 mm in diameter representing the rebars was built up. The concrete modelled here was assumed heterogeneous and the rebars impenetrable. Based on the mass conservation equation and Nernst-Planck equation (Li *et al.*, 2015; Liu *et al.*, 2015; Xia and Li, 2013) coupled with Gauss' Law, diffusion and electric migration were considered in the model.

The electric potential was 24 V at anode and 0 at cathode. The influence of temperature is reflected on the following four aspects.

Binding effect

The previous studies showed that the binding capacity of ions is relative with temperature, which could be illustrated with Arrhenius equation (Dousti and Shekarchi, 2015; Hussain and Rasheeduzzafar, 1993; Jakobsen *et al.*, 2000; Maslehuddin *et al.*, 1997; Oh and Jang, 2007; Panesar and Chidiac, 2011; Roberts, 1962; Saetta *et al.*, 1993; Song *et al.*, 2007; Xu *et al.*, 2016) as

$$C_b(C, T) = C_b(C, T_0) e^{\frac{E_b}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (1)$$

where $C_b(C, T)$ (mol/m³) is the concentration of bound chloride when the free chloride concentration is C (mol/m³) at the temperature T (K), $C_b(C, T_0)$ (mol/m³) is the concentration of bound chloride when the free chloride concentration is C (mol/m³) at the reference temperature T_0 (K), E_b (kJ/mol) is the binding activation energy.

Diffusion coefficient

The diffusion coefficient of ions has a relationship with temperature in the form (Colleparidi *et al.*, 1972; Dousti *et al.*, 2013; Page *et al.*, 1981; Saetta *et al.*, 1993; So *et al.*, 2014)

$$D(T) = D_0 e^{\frac{E_D}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} \quad (2)$$

where $D(T)$ (m²/s) is the diffusion coefficient of ions at the temperature T (K), D_0 (m²/s) is the diffusion coefficient of ions at the reference temperature T_0 (K), E_D (kJ/mol) is the diffusion activation energy.

Migration flux

According to the Nernst-Planck equation, the migration flux J_m could be calculated as

$$J_m = -\frac{1}{T} \left(\frac{zDF}{R} \nabla \Phi \right) C \quad (3)$$

where $F = 9.648 \times 10^{-4}$ (C/mol) is the Faraday constant, $R = 8.314$ (J/(mol·K)) is the ideal gas constant, Φ is the electric potential.

It is obvious that the migration flux is directly influenced by the temperature.

Electrolyte concentration

Saturated calcium hydroxide, of which the dissolving capacity is found apparently affected by temperature is ordinarily used as the electrolyte at the anode and assumed as the initial pore solution. Therefore, the concentration condition at the anode and initial condition would be different at the different temperatures, causing an influence on the ECR efficiency.

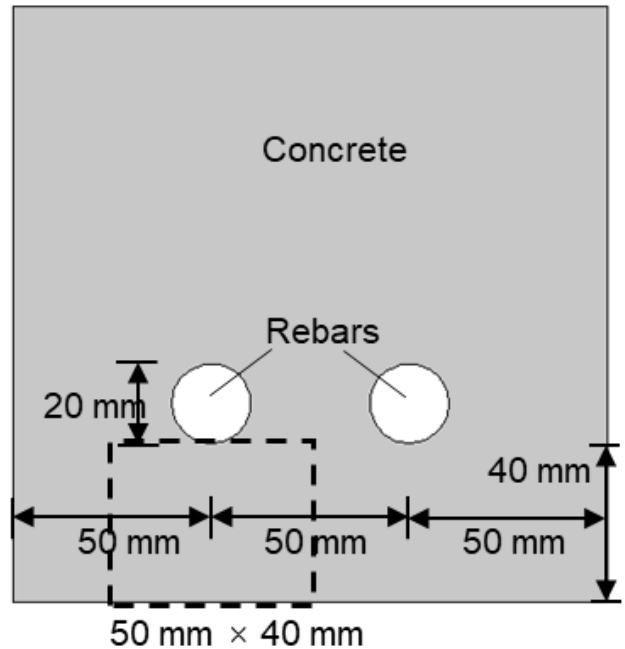


Fig. 6. 2-D Schematic of the Concrete Specimen for Simulation

3.2 Results, Comparisons and Discussions

The simulations of ECR treatment for 15 days at the temperatures of 0 °C, 20 °C and 50 °C were performed. The counter map of the remained chloride concentrations in the area of dashed rectangle (see Fig. 6) was plotted as Fig. 7. Fig. 8 showed the relative error of simulation and experiment which was calculated as the ratio of deviation to intitle concentration.

The concentrations in the most of concrete were larger than 50 mol/m³ at 0 °C while the ones at 20 °C were less than 50 mol/m³. The remained chloride concentrations were less than 10 mol/m³ at 50 °C, meaning that the ECR efficiency was quite considerable.

Though the simulation results were a little different from the experimental ones due to the impact of the aggregate and pore distribution which was not considered in the numerical model, the absolute values of relative error in most areas were less than 30%, which proved the reliability of the numerical model. Moreover, the familiar tendency could be found in both simulation results and experimental results that the remained chloride concentrations decreased with the temperature increasing.

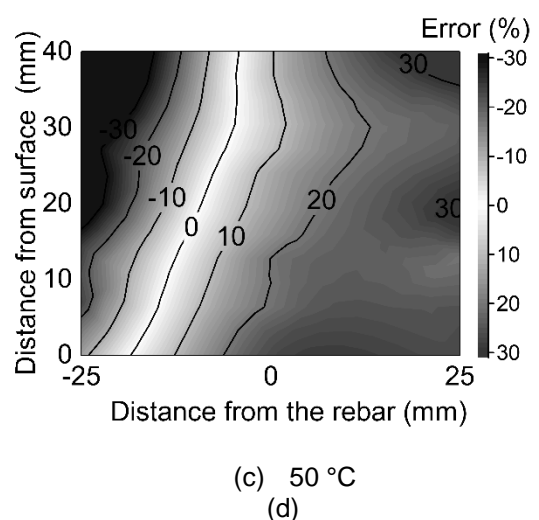
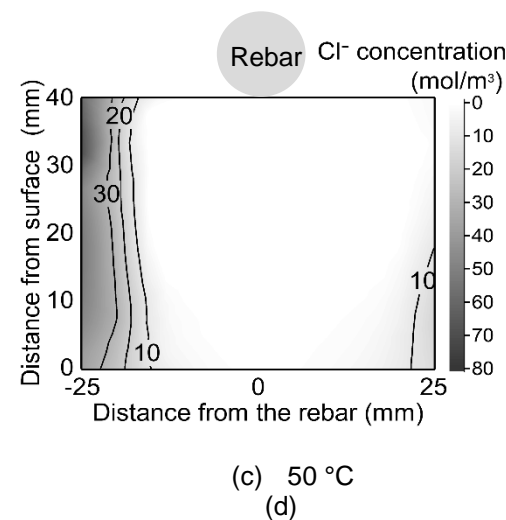
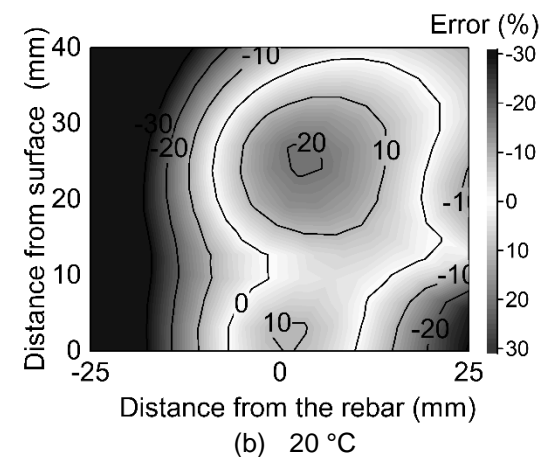
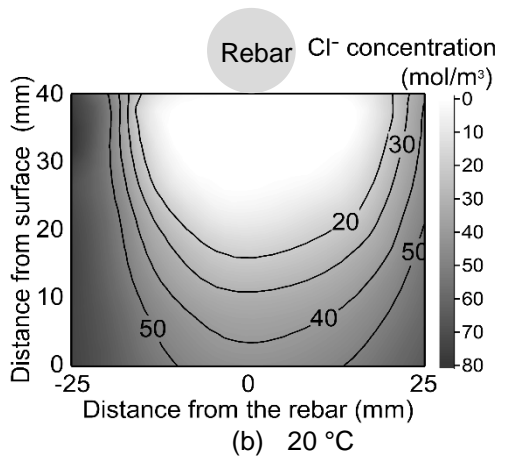
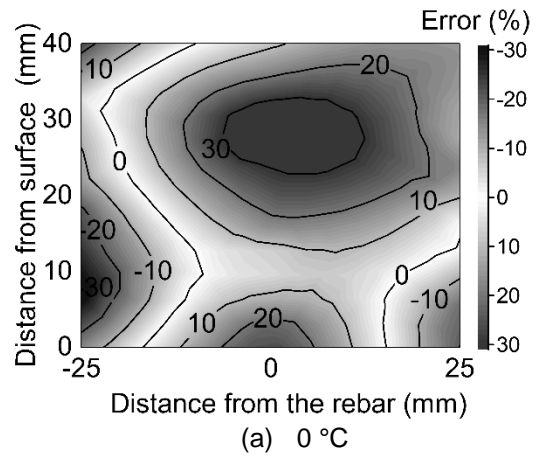
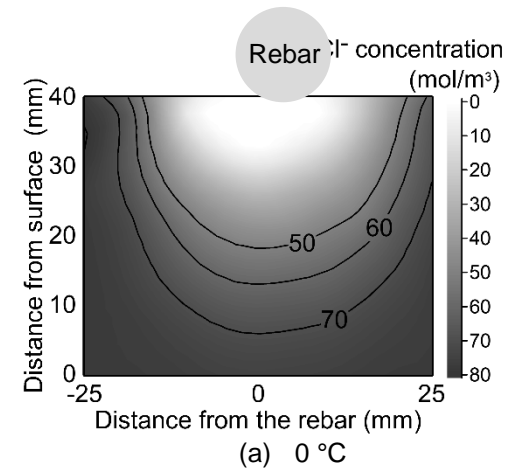


Fig. 7. Chloride Distributions for Various Temperatures after ECR Simulation

Fig. 8. Relative Error of Simulation and Experiment

4.0 CONCLUSIONS

This paper has studied the difference of chloride distributions in concrete at the different temperatures. Based on the experimental and simulation results, the following conclusions can be drawn.

(1) The ECR treatment is not recommended to be applied directly when temperature is as low as -

10°C since the electrolyte in concrete would freeze, leading to a very low current density.

(2) The temperature has a considerable impact on ECR treatment. The remained chloride concentrations decreased remarkably when the temperature rose to 20 °C and 50 °C from 0 °C.

(3) The influence of temperature is larger at a relatively lower temperature. The difference of remained chloride concentrations between 0 °C

and 20 °C was much larger than that between 20 °C and 50 °C.

Acknowledgement

This work was supported by the Natural Science Foundation of China (51778566, 51408537, 51638013), the Key Project supported by Zhejiang Provincial Natural Science Foundation of China (LZ16E080002), the Technology Project of State Grid Zhejiang Electric Power Corporation (5211DS16001N), Scientific Program for traffic engineering construction of Transport Department of Zhejiang Province (2015J02) and the Fundamental Research Funds for Central Universities (GF10Z01EF1).

References

- Andrade, C., J. M. Diez, A. Alaman, and C. Alonso, 1995, Mathematical-modeling of electrochemical chloride extraction from concrete: cement and concrete research, v. 25, p. 727-740.
- ASTM, 2015, Standard test method for water-soluble chloride in mortar and concrete, in C1218/C1218M-15, ASTM, ASTM[®]Editors., ASTM International: West Conshohocken, PA.
- Banfill, P. F. G., 1997, Re-alkalisation of carbonated concrete — Effect on concrete properties: *Construction & Building Materials*, v. 11, p. 255-258.
- Chang, C. C., W. Yeih, J. J. Chang, and R. Huang, 2014, Effects of stirrups on electrochemical chloride removal efficiency: *Construction and Building Materials*, v. 68, p. 692-700.
- Collepari, M., A. Marcialis, and R. Turriziani, 1972, Penetration of Chloride Ions into Cement Pastes and Concretes: *Journal of the American Ceramic Society*, v. 55, p. 534-535.
- Dhir, R. K., M. R. Jones, and A. E. Elghaly, 1993, PFA concrete: Exposure temperature effects on chloride diffusion: *Cement & Concrete Research*, v. 23, p. 1105-1114.
- Dousti, A., R. Rashetnia, B. Ahmadi, and M. Shekarchi, 2013, Influence of exposure temperature on chloride diffusion in concretes incorporating silica fume or natural zeolite: *Construction and Building Materials*, v. 49, p. 393-399.
- Dousti, A., and M. Shekarchi, 2015, Effect of exposure temperature on chloride-binding capacity of cementing materials: *Magazine of Concrete Research*, v. 67, p. 821-832.
- Elsener, B., and U. Angst, 2007, Mechanism of electrochemical chloride removal: *Corrosion Science*, v. 49, p. 4504-4522.
- Garces, P., M. de Rojas, and M. A. Climent, 2006, Effect of the reinforcement bar arrangement on the efficiency of electrochemical chloride removal technique applied to reinforced concrete structures: *CORROSION SCIENCE*, v. 48, p. 531-545.
- Guo, Y., and J. Gong, 2011, Study of electrochemical chloride extraction of reinforced concrete: *Journal of Taiyuan University of Technology(Social Sciences Edition)*, p. 588-592.
- Hussain, S. E., and Rasheeduzzafar, 1993, Effect of temperature on pore solution composition in plain cements: *Cement & Concrete Research*, v. 23, p. 1357-1368.
- Jakobsen, H. J., J. Skibsted, M. Korzen, and O. M. Jensen, 2000, Influence of cement constitution and temperature on chloride binding in cement paste: *Advances in Cement Research*.
- Jiang, Z., 2008, A state-of-the-art review on electrochemical realkalisation of carbonated concrete structures: *Materias Review*, p. 78-81.
- Jin, W., and Y. Zhao, 2014, durability of concrete structures: Beijing, Science Press, 371-380 p.
- Li, L., D. Easterbrook, J. Xia, and W. Jin, 2015, Numerical simulation of chloride penetration in concrete in rapid chloride migration tests: *Cement and Concrete Composites*, v. 63, p. 113-121.
- Liu, Q., J. Yang, J. Xia, D. Easterbrook, L. Li, and X. Lu, 2015, A numerical study on chloride migration in cracked concrete using multi-component ionic transport models: *Computational Materials Science*, v. 99, p. 396-416.
- Maslehuddin, M., C. L. Paget, and Rasheeduzzafar, 1997, Temperature effect on the pore solution chemistry in contaminated cements: *Magazine of Concrete Research*, v. 49, p. 5-14.
- Němeček, J., J. Kruis, T. Koudelka, and T. Krejčí, 2018, Simulation of chloride migration in reinforced concrete: *Applied Mathematics and Computation*, v. 319, p. 575-585.
- Oh, B. H., and S. Y. Jang, 2007, Effects of material and environmental parameters on chloride penetration profiles in concrete structures: *Cement & Concrete Research*, v. 37, p. 47-53.
- Page, C. L., N. R. Short, and A. E. Tarras, 1981, Diffusion of chloride ions in hardened cement pastes: *Cement & Concrete Research*, v. 11, p. 395-406.
- Panesar, D. K., and S. E. Chidiac, 2011, Effect of Cold Temperature on the Chloride-Binding Capacity of Cement: *JOURNAL OF COLD REGIONS ENGINEERING*, v. 25, p. 133-144.
- Roberts, M. H., 1962, Effect of calcium chloride on the durability of pre-tensioned wire in prestressed concrete*: *Magazine of Concrete Research*, v. 14, p. 143-154.
- Saetta, A. V., R. V. Scotta, and R. V. Vitaliani, 1993, Analysis of chloride diffusion into partially saturated concrete: *Aci Materials Journal*, v. 90, p. 441-451.
- So, H., S. Choi, K. Seo, C. Seo, and S. So, 2014, The properties of chloride ion diffusion of concrete under high temperature conditions, with implications for the storage of spent nuclear fuel in concrete casks: *KSCE Journal of Civil Engineering*, v. 18, p. 2227-2233.

- Song, H. W. S. W., C. H. L. H. Lee, M. S. J. S. Jung, and K. Y. A. Y. Ann, 2007, Development of chloride binding capacity in cement pastes and influenc...: Canadian Journal of Civil Engineering, v. 35, p. 1427-1434.
- Tang, L., 1996, Chloride Transport in concrete - Measurement and Prediction, Chalmers University of Technology, Goteborg.
- Xia, J., and L. Li, 2013, Numerical simulation of ionic transport in cement paste under the action of externally applied electric field: Construction and Building Materials, v. 39, p. 51-59.
- Xu, J., Y. Song, L. Jiang, W. Feng, Y. Cao, and W. Ji, 2016, Influence of elevated temperature on release of bound chlorides from chloride-admixed plain and blended cement pastes: Construction and Building Materials, v. 104, p. 9-15.
- Yodsudjai, W., and W. Saelim, 2014, Influences of Electric Potential and Electrolyte on Electrochemical Chloride Removal in Reinforced Concrete: Journal of Materials in Civil Engineering, v. 26, p. 83-89.