Effect of Current Modes on Electrochemical Chloride Extraction Treatments for Concrete

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Abstract. *The current mode plays an important role in the Electrochemical Chloride Extraction (ECE) treatment for concrete. In this study, the experiments were conducted to investigate how the ECE process would be affected by different current modes (continuous and intermittent current modes). The results showed that there were remaining amounts of chloride ions that were hard to be removed by both current modes. Additionally, the porosity under the two current modes showed the same upward trend compared to the initial value, and the chloride diffusion coefficient increased by 1 - 2 times. Also, the chloride-contaminated concrete subjected to the continuous current mode had a higher cumulative chloride extraction content than that subjected to the intermittent mode. The intermittent current mode could not increase the effectiveness of extracting chloride when the current density was not greater than 3 A/m^2 and the on-off ratio was not less than 3.2.*

Keywords: *Electrochemical Chloride Extraction, current mode, porosity, free chloride, bound chloride*

1 Introduction

Reinforced concrete (RC) is a composite material frequently used in modern buildings and infrastructures, in which steel bars are embedded in the concrete to resist forces. However, due to the porous characteristic of concrete materials, harmful factors such as chlorides in the environment can infiltrate into the concrete, increasing the risk of steel corrosion (Gu et al. 2020, Chen et al. 2019, Zhang et al. 2016). Existing RC constructions in coastal areas, in particular, are at risk of degradation due to corrosion by chloride (Zhou et al. 2018, Zhang et al. 2016, Jiang et al. 2022). In order to avoid losses caused by structural degradation, action must be taken to prevent chloride penetration and corrosion.

Electrochemical Chloride Extraction (ECE) is a non-distractive approach for postponing corrosion initiation by applying an electric field between the reinforcement and the outer surface of the concrete to remove chloride ions from chloride-containing RC members (Song et al. 2022). In the process of ECE, the current mode is one of the key factors affecting chloride extraction (Bouteiller et al. 2022, Jiang et al. 2023). By setting the current cycle in ECE process, the current-off periods in the process are able to shift the chemical balance to free chloride ion, which has the potential to improve the chloride extraction efficiency (Saraswathy et al. 2018). Therefore, it is of great significance to compare and evaluate the effectiveness of current mode on ECE efficiency in both theory and engineering practice.

However, the study on the effect of the current modes (continuous and intermittent) on ECE

process is still limited. In this work, Electrochemical Chloride Extraction tests under different current modes were conducted, and the progress of each test was monitored throughout the whole process. Free chloride ion and total chloride ion were profiled in all specimens. By monitoring the whole progress, the effects of different current modes on the chloride extraction were compared.

2 Electrochemical chloride extraction test

Cylindrical mortar specimens with a diameter of 110 mm and a height of 200 mm were cast for ECE tests. The mix proportion is listed in Table 1. Deionized water and Ordinary Portland cement were used with a water-cement ratio of 0.53. ISO standard sand was used as fine aggregates. The mortar was pre-mixed with 3% sodium chloride (NaCl) per unit mass of cement. After curing, the top and bottom surfaces were sealed with epoxy resin, and only the lateral surface was exposed for ion transfer. Saturate calcium hydroxide solution was used as the electrolyte.

Table 1. Mortar mix proportion.

Cement type	W/C	Cement	Water	Sand	NaCl
P.O 42.5	0.53	480 kg/m^3	254 kg/m^3	1200 kg/m^3	23.7 kg/m^3

Continuous and intermittent current modes were designed for the ECE tests. Current density of both groups was set as 3 A/m^2. In continuous current group (Group A), specimens were power-on uninterrupted from the beginning to the end of the test. While in the intermittent current group (Group B), the specimen underwent a current cycle of 3 days of power-on and 2 days of power-off. The total ECE duration was 56 days and 63 days respectively (including the power-off period in Group B). The arrangement of ECE tests is shown in Table 2. In order to gain the chloride distribution ions during the ECE process, a series of specimens were designed for chloride profiling at specified times sequentially. The specimen that had been terminated the test for chloride profiling was not be reused for the ECE test.

Table 2. Arrangement of ECE tests.

Specimen	Current mode	ECE duration (day)	Specimen	Current mode	ECE duration (day)
A-0	0	0	B-1-5	Int. 3A/m^2	5
A-1	Cont. 3A/m^2	7	B-2-3	Int. 3A/m^2	8
A-2	Cont. 3A/m^2	14	B-2-5	Int. 3A/m^2	10
A-4	Cont. 3A/m^2	28	B-4-3	Int. 3A/m^2	18
A-6	Cont. 3A/m^2	42	B-4-5	Int. 3A/m^2	20
A-8	Cont. 3A/m^2	56	B-9-3	Int. 3A/m^2	43
A-C-4	0	28	B-9-5	Int. 3A/m^2	45
A-C-8	0	56	B-13-3	Int. 3A/m^2	63
B-0-0	0	0	B-13-5	Int. 3A/m^2	65
B-1-3	Int. 3A/m^2	3	B-C-12-5	0	65

*_Cont._ represent Continuous current mode, _Int._ represents Intermittent current mode. In the intermittent mode, the current-off periods are included in the _ECE duration_.

Following ECE tests, total and free chloride ion contents were determined by the

potentiometric titration method. The current was cut off once a specimen had achieved the specified ECE treatment duration. Before sampling, the specimen was sliced into eight circular samples. Due to the influence of side effects, two samples at both ends were discarded, leaving only the other middle samples for chloride profiling. Then, mortar powder was obtained by drilling along the radius direction using a milling machine. The detailed sampling process is shown in Figure 1.
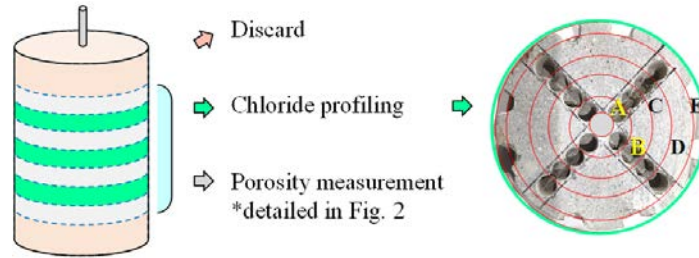

Figure 1. Sampling process for chloride profiling.

The contents of total and free chloride ions were determined before, during, and after the ECE process. In this study, the ZDJ-4B Potentiometric Titrator was used for chloride profiling. All chloride contents in this work were based on JGJ/T 322-2013 and were stated as percentages of mortar mass (JGJ/T 322-2013).

The porosities φ before and after ECE test were tested by water saturation method, as shown in Figure 2. In order to measure the porosity at different radii, concentric rings were drilled with the centroid of the slice. For porosity determination, the following masses m_i (g) were measured. (I) the original mass of the water container, m_1; (II) the mass of pre-saturated ring with water container, m_2; (III) the mass of the system when the ring was lifted with a thin wire to make it completely suspended in the water, m_3; (IV) the mass of oven-dried ring, m_4. The porosity of the ring can be calculated according to equation (1).

$$\varphi = \frac{m_2 - m_1 - m_4}{m_3 - m_1 - m_s} \tag{1}$$

where, m_s is the mass of the steel bar in the inner ring (g).
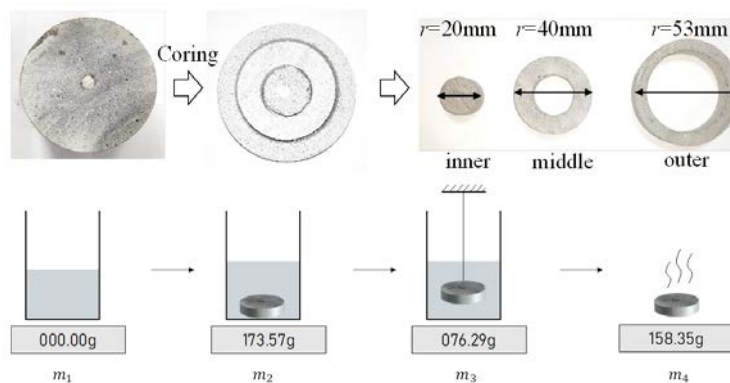

Figure 2. Porosity measurement (Water saturation method).

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3 Results and discussion

3.1 Dynamic features of chloride distribution

In the study, the design pre-mixed quantity of chloride was 3% of the cement mass, which accounted for 0.797% of saturated mortar, and 0.887% of drying mortar. The distribution of total chloride ions in initial state of the specimens is shown in Figure 3. The dash-dotted line in the figure is the chloride content of the drying mortar and the dash lines represent the chloride content of saturated mortar.
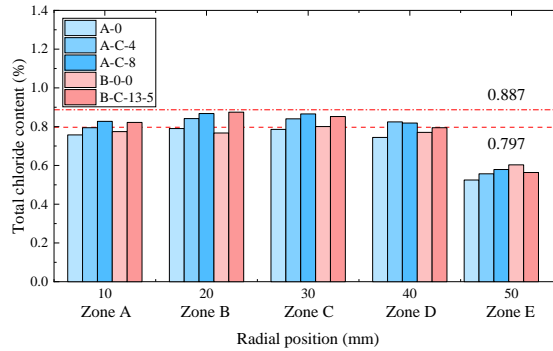

**Figure 3**. Initial chloride distribution of the specimens.

As illustrated by Figure 3, the total chloride ion contents on the specimen's surface (Zone E) were lower than the other zones, owing to chloride ion loss on the surface during the curing period, whereas the average total chloride content in Zones A to D was 89.6%, 93.4%, 93.5%, and 89.1% of the theoretical value, respectively, which were within the margin of error.

Figure 4 shows the free and total chloride distribution in real-time of the entire ECE process for two current modes.
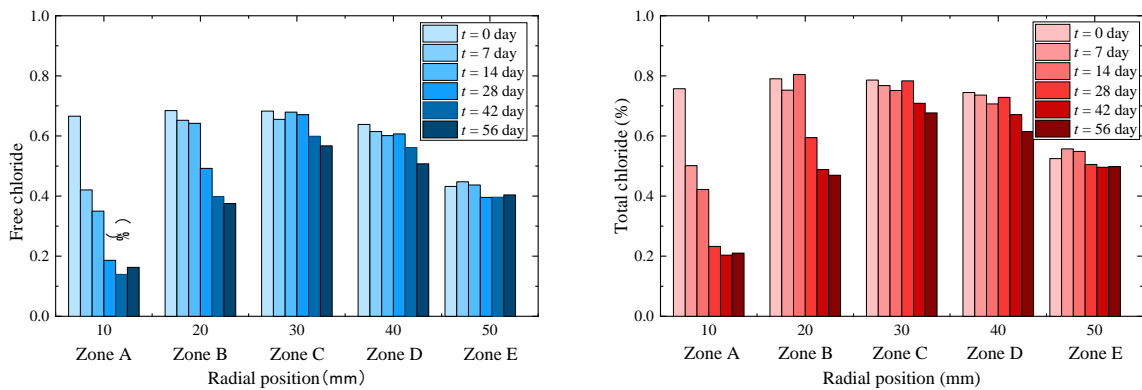
(a) Free chloride, Continuous current mode

(b) Total chloride, Continuous current mode
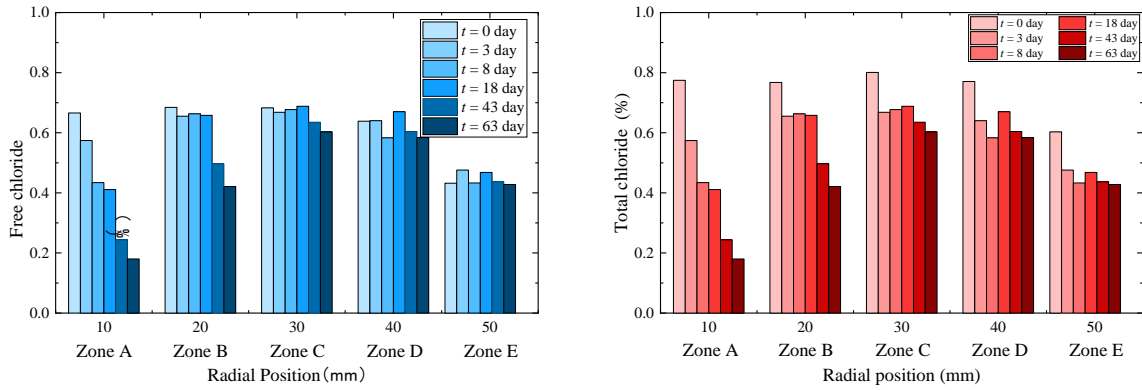
(c) Free chloride, Intermittent current mode   (d) Total chloride, Intermittent current mode
Figure 4. Free and total chloride distribution in entire ECE process.

As shown in Figure 4, in general, the trends of chloride ion distributions in the two current modes were consistent during the entire ECE process. In both cases, the total chloride content was slightly larger than the free chloride content in the same sample, but the change regulation of both was essentially the same. The chloride content in Zone A (reinforcement side) decreased sharply during the first four weeks after electrification, but gradually during the final four weeks. This was owing to the continual accumulation of hydroxide ions produced by cations and electrode reactions on the reinforcing side, which resulted in greater conductivity and a decrease in the potential gradient in this area. On the other hand, the remaining chloride ions may be mostly due to physical adsorption or chemical binding and therefore unable to migrate under the influence of an electric field.

During the 2nd to 6th week of ECE processing, the chloride content in Zone B decreased, but it was lower than that of Zone A. This is because Zone B's chloride content can only decrease when Zone A's chloride content reaches a certain level, and the amount of chloride moving from Zone A to Zone B is less than the amount moving from Zone B to Zone C. This same phenomenon, known as hysteresis, also occurs in Zones C, D, and E.

3.2 Regional efficiency of Electrochemical Chloride Extraction

Figure 5 shows the proportion of free chloride ions at the end of current-on periods (B-t-3) and the end of current-off periods (B-t-5) in each cycle of intermittent current mode.
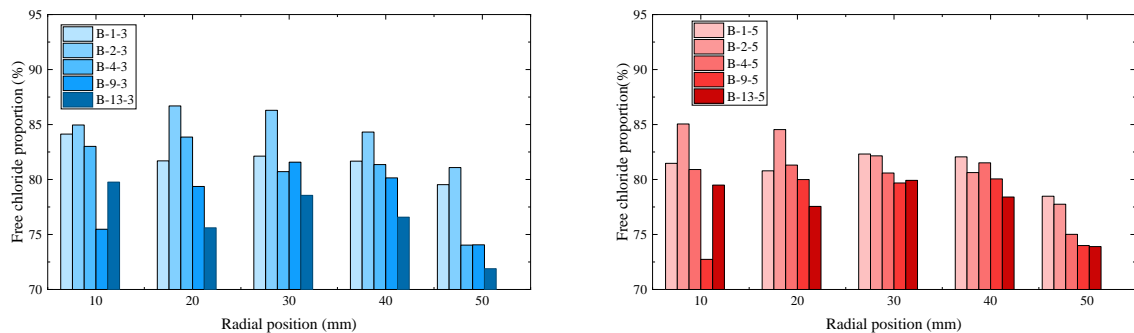

Figure 5. The percentage of free chloride content of intermittent current mode.

As shown in Figure 5, for the index of the percentage of free chloride ion content, the range of which during the current-on period was 71.9% to 86.7%, with an average of 80.6%, while in the current-off period was 72.7% to 88.3%, with an average of 80.1%. Therefore, it can be considered that when the on-off ratio of current cycle is no less than 3:2, the free chloride percentage of current-off is not significantly different from that of current-on.

Figure 6 shows the distributions of chloride ion content in each zone under the same current duration. There is no significant difference in chloride ion content between the two current modes when the current duration is the same. In other words, the binding reaction transition does not limit the efficiency of the ECE process. There are two plausible explanations. The first is that the binding reaction's conversion rate is more than or equal to the migration rate, and the equilibrium can be reached without current-off period. Second, the conversion rate is substantially lower than the migration rate, and the unbalanced condition does not significantly recover during the current-off periods.
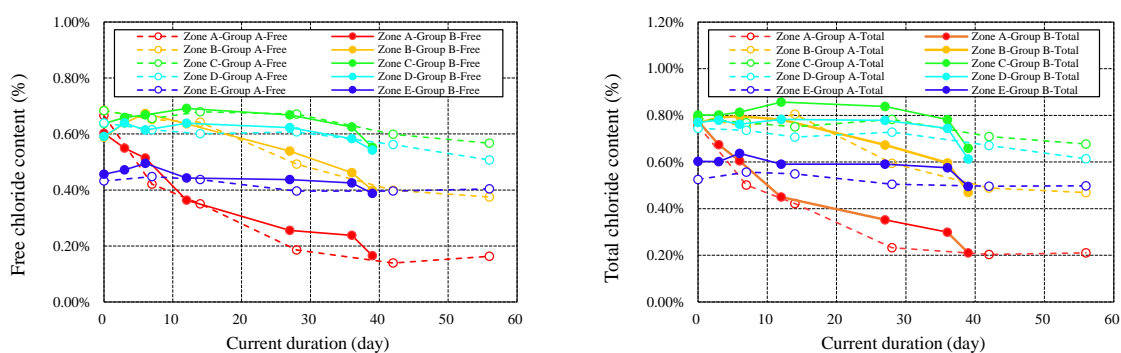

Figure 6. Comparison of chloride content in different zones under same current duration.

The cumulative chloride content in the electrolyte for the two modes with the same current duration is shown in Figure 7. The chloride extraction rate of continuous current group A is larger than that of intermittent current group B. This could be due to the fact that in the current on-off cycles, the chloride discharge rate always increased from zero with each power-up, resulting in a reduction in the effective power-up time of Group B.
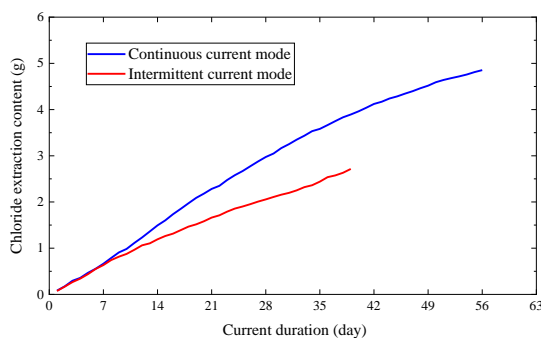

Figure 7. Cumulative chloride content in the electrolyte.

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3.3 Porosity distribution

The porosity of different areas of the specimen measured by the water saturation method is shown in Figure 8. Before ECE process, the porosity of the inner ring was slightly higher than that of the middle ring and the outer ring, with an amplitude of around 0.01 to 0.015, which might be caused by the reinforcing side wall effect. For inner rings, the porosity tends to rise in continuous current mode, increasing by 0.005 to 0.01, while the porosity essentially stays constant under intermittent current mode. For the middle ring, the porosity changes were not significant under the two modes. For the outer ring, there is a slight decrease in porosity under both modes, with a decrease of about 0.01 to 0.23. In general, the porosity of the specimen changes varied in different locations under the two modes, the change amplitude ranged from 0.215 to 0.245. The change rate of chloride diffusion coefficient caused by porosity change in the ECE process was about 1 - 2.
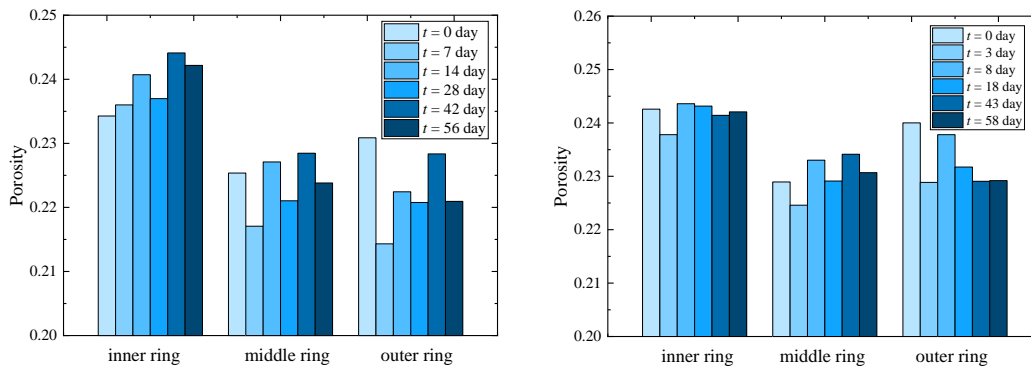

Figure 8. Porosity distribution during the ECE process.

4 Conclusions

- In the cylindrical mortar specimen, the chloride ion close to the reinforcement is first removed, but as the chloride ion content lowers to a certain level, the removal rate falls down sharply.
- The distributions of chloride ions in the whole ECE process under continuous and intermittent current modes are essentially consistent when the current density is not greater than 3 A/m^2 and the on-off ratio is not less than 3:2. The intermittent current mode cannot increase the efficiency of chloride extraction.
- The specimen's porosity will alter during the ECE process, changing the diffusion coefficient and impacting the ion transport process. At the current density of 3 A/m^2 for 56 days, the change range of porosity is 0.215 to 0.245, and the change ratio of chloride diffusion coefficient may reach 2.

References

Bouteiller, V., Tissier, Y., Marie-Victoire, E., Chaussadent, T., and Joiret, S. (2022). *The application of electrochemical chloride extraction to reinforce concrete-A review*, Construction and Building Materials, 351, 128931.

Chen, J. Y., Zhang, W. P., and Gu, X. L. (2019). *Modeling time-dependent circumferential non-uniform corrosion of steel bars in concrete considering corrosion-induced cracking effects*, Engineering Structures, 201, 109766.

Gu, X. L., Dong, Z., Yuan, Q., and Zhang, W. P. (2020). *Corrosion of Stirrups under Different Relative Humidity Conditions in Concrete Exposed to Chloride Environment*, Journal of Materials in Civil Engineering, 32(1), 04019329.

JGJ/T 322-2013 (2013). *Technical specification for test of chloride ion content in concrete*, China National Standard.

Jiang, C., Ding, H., Gu, X. L., and Zhang, W. P. (2022). *Failure mode-based calculation method for bending bearing capacities of normal cross-sections of corroded reinforced concrete beams*, Engineering Structures, 258, 114113.

Jiang, C., Song, C., Gu, X. L., Zhang, Q., and Zhang, W. P. (2023). *Modeling electrochemical chloride extraction process in cement-based materials considering coupled multi-ion transports and thermodynamic equilibriums*, Journal of Cleaner Production, 401, 136778.

Saraswathy, V., Lee, H., Karthick, S., and Kwon, S. (2018). *Extraction of chloride from chloride contaminated concrete through electrochemical method using different anodes*, Construction and Building Materials, 158:549-562.

Song, C., Jiang, C., Gu, X. L., Zhang, Q., and Zhang, W. P. (2022). *Calibration analysis of chloride binding capacity for cement-based materials under various exposure conditions*, Construction and Building Materials, 314: 125588.

Zhang, H. F., Zhang, W. P., Gu, X. L., Jin, X. Y., and Jin, N. G. (2016). *Chloride penetration in concrete under marine atmospheric environment - analysis of the influencing factors*, Structure and Infrastructure Engineering, 2(11), 1428-1438.

Zhang, W. P., Ye, Z. W., and Gu, X. L. (2016). *Effects of stirrup corrosion on shear behaviour of reinforced concrete beams*, Structure and Infrastructure Engineering, 13, 1081-1092.

Zhou, B. B., Gu, X. L., Guo, H. Y., Zhang, W. P., and Huang, Q. H. (2018). *Polarization behavior of activated reinforcing steel bars in concrete under chloride environments*, Construction and Building Materials, 164, 877-887.