Voltage on the distribution of the residual chlorine ion of the concrete after the electrochemical dechlorination treatment

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Abstract. This paper utilizes 60V stable voltage power, saturated calcium hydroxide solution, titanium mesh anode to analyze the influence of the mineral admixtures, applied voltage and electrolyte solution on the residual chloride ions distribution after 14 consecutive days’ test of the electrochemical chloride extraction of the cylinder concrete. The results show that after electrochemical chloride extraction, the residual chloride ions content in concrete shows increasing trend from inside to outside of the reinforced interface, with the least at internal layer and the most at external layer and there are 2-3.5 times differences between internal layer and external layer. The difference between the internal layer and external layer increases with the increase of the chloride extraction voltage.

1 Introduction
Recent years, because of the corrosion of reinforcement, the concrete structure’s performance declines, which causes the service life not to meet design requirements and become disabled. This has been a major problem of science and technology in the civil engineering territory [1-2]. There are several factors which could cause the corrosion of concrete reinforcement. From the current engineering damage statistics, the main reason that causes reinforcement corrosion is sort of chlorine salt invasion [3]. Electrochemical chloride extraction [4] refers to the process of extracting chloride salt and other harmful components through applied electric filed in the concrete protection layer without damaging it and then passivating the corroded steel surface. It is an efficient and low cost technology for the restoration of reinforced concrete. Since 1990’s, developed European and American countries have started spending energy on the research in this field[5], but they mainly focused on the influence of dechloride’s effect caused by the external factors such as the electrochemical parameter [6-8]. However, only few concentrate on the influence of the concrete mix proportion on the efficiency of the electrochemical chloride extraction. This paper applies the homemade test units of electrochemical chloride extraction, to analyze the influence of different water-cement ratio on the efficiency of electrochemical chloride extraction according to the test of the electric current through the concrete specimen, the chloride ion discharge, and residual chloride ion content in the same electric field.

2 Experiment

2.1 Raw material and mixing proportion of concrete
Using both P. O42.5 cement of Harbin cement co., Yatai Group and II grade fly ash of Harbin No.3 Thermal Power, water requirement ratio is 97%. Anshan iron and steel production of blast furnace slag, its density is 2.86 g/cm3, specific surface area of 390 m2 / kg. Norway's company
production of Micronesia silica fume, the average particle size of 0.1 μm, specific surface area of 1.5 x 104 m2 / kg, density: 2.26 g/cm3. Choose the limestone rubble, particle size grading in 5 ~ 25 mm, crushing index was 4.8%, the needle flake content 3%; Fine aggregate used river sand of Songhua river, fineness modulus of Mx = 2.82, belong to medium sand, II district. The Shanghai Huawang company's Mighty 100 high efficiency water reducing agent, recommended dosage 0.7 to 1.2% of the total weight for the gelled material. Ordinary steel reinforcement for 8 mm diameter. Sodium chloride for industrial pure product, NaCl content is more than 96%.

2.2 Specimens
Φ100 x 150 mm cylindrical concrete specimen was used, and a Φ 10 mm steel bar was inserted into the specimen along the direction of the axis., the relative position of steel reinforcement and concrete specimen is shown in figure 1. Before concrete formed, steel was made 15mm long and soaked in three ammonia solution to remove the surface rust; After the surface dried, the steel outside of the concrete was covered with surface coating of epoxy resin to prevent this part of the steel being corroded during the concrete curing. Then the processed reinforcement device was fixed well in the special processed mold, to ensure that the coating with epoxy resin reinforced part of the dew on the outside of the concrete, the rest of the concrete axial center location. Concrete specimen was taken out of the mold when it forms after 1 day and then put in a standard curing room for maintenance, wrapped in plastic to prevent the loss of chloride salt in the concrete due to water conservation. To 28 day age, the specimens are retrieved from the room, and then are dealt with electrochemical chloride extraction treatment.

2.3 Method
Homemade test apparatus (as shown in Fig. 2) is utilized for the electrochemical chloride treatment of each concrete. During this experiment, saturated calcium hydroxide solution, 0.1mol/L Na3BO3 solution and tap water are used as the electrolyte respectively. Titanium mesh anode of high corrosion resistance is chosen. The external source is 20V, 40V, and 60V stable AC power. And the rheostat connections are fixed 10 Ω resistance. By measuring the voltage of the fixed resistance connected on the reinforced ends, the current value across the concrete specimens can be converted. Change the electrolyte solution every 2 days. The electrochemical chloride extraction costs 14 days.

After the concrete dechloridation, take out the specimen and remove the residual precipitation of crystal on the surface. Cut the cylinder concrete specimen radially from the reinforcement external diameter into two parts, with the profile shown as Fig. 3. Cut steel trisection along axial direction, from up to down number I, II, III, IV respectively; divide concrete radially into inner, middle, and outer 3 layers. Take concrete samples at the intersection point of layer and layer, which refers to the black point in the figure. Choose mortar instead of coarse aggregate and large granule fine aggregate. Then grind the sample into powder as the fineness of cement and weigh. Because the purpose of this experiment is to measure the related soluble ion concentration, choose the distilled water to soak and dissolve powder sufficiently. A week later, utilize precise ion meter to measure the specimens’ chloride ion, sodium ion and potassium ion content, and convert into ion concentration of relevant position.
3 Results and Analysis

The influence on the residual chloride ion

Three kinds of specimens are made by changing mix proportion of 0.45, 0.38, 0.32 and using saturated Ca(OH)\textsubscript{2} solution as electrolyte solution. The time for dechlorination is 28 days. The influence of voltage on the residual chloride in different layers after dechlorination is shown in figure 4. The influence of voltage on the distribution of residual chloride in vertical direction is shown in figure 5.

![Diagram](image1)

**Fig. 1 Immersed steel in concrete specimen**

![Diagram](image2)

**Fig. 2 Experimental ECE set-up.**

![Diagram](image3)

**Fig. 3 Schematic diagram of the specimen after Cl\textsuperscript{-} has been extracted**

![Graph](image4)

**Fig. 4 Influence of the potential on the concentration of the Cl\textsuperscript{-} after electrochemical chloride extraction**

a) W/C = 0.45

b) W/C = 0.38

c) W/C = 0.32
Figure 4 compares the influence of different voltage on different water-cement ratio specimens’ to analyze the residual chloride ion distribution gradient after dechlorination. From the figure, after the electrochemical chloride extraction process, chloride ion content on the external layer of concrete is obviously higher than the internal layer of concrete. The higher the applied voltage, the lower concentration of the residual chloride on the internal layer is, and the better effect of dechloridation is. This phenomenon on one hand macroscopically reflects the character that the voltage influences the internal chloride ion of concrete moving out to external layer. From figure 4, it is also easy to find out the higher voltage, the lower residual chloride ion content on each layer is, and the better effect of dechloride is. On the contrary, the lower voltage for dechloride, the higher residual chloride ion content on each layer is, the worse effect of dechloride is. For the specimens which have lower water-cement ratio, there is only little difference between dechloride that uses 40V and 60V voltage.

According to figure 4, analyzing the chloride concentration of the internal layer of three kinds of concrete after dechlorination, it is easy to conclude that the higher voltage, the lower residual chloride ion content near the rebar region is. For the specimens which have lower water-cement ratio (W/C are 0.38 and 0.32), the result under 60V voltage is higher than that under 40V voltage, but the difference is quite small. However, for the specimens which have W/C as 0.45 ratio, the results are much different among the conditions under three voltages.

Figures 5 compares the residual chloride ion distribution of upper layer and lower layer of concrete after dechlorination under different applied voltages. From the figure, residual chloride ion content is the highest at the IV layer along axial direction, and the lowest content at the I, III layers. This is because the lower layer of the IV layer is farthest away from rebar, and keeps in contact with the vessel during the experiment, for this reason, the tunnel cannot be developed properly which will lead the stack of the chloride ion, and chloride ion content obviously higher at the IV layer of concrete. The chloride ion distribution on the I, II, III layers of every sample are almost the same. For each layer, there is a stronger regularity of the residual chloride ion distribution for different distances from the steel: chloride ion content increases from internal to external in the specimens. Chloride content is almost the same for each layer of concrete. However, sometimes there are some little differences. So it is easy to conclude that the distribution of chloride after dechloride has little relationship with the vertical direction, while it is influenced a lot by the distance from the rebar. So we should consider how to prevent the residual chloride ion at the external layer of concrete from re-corroding internal region of concrete.

According to the data in figure 4, entire dechloride efficiency and the efficiency of dechloride near the rebar of each specimen can be calculated. Kinds of parameters contrast condition are shown in figure 5.

Fig.5 Influence of the potential on the concentration of the Cl' in longitude direction after electrochemical chloride extraction
6 and figure 7. From the figures, three kinds of water-cement ratio are analyzed and compared with each other under the voltage of 20V 40V 60V respectively after 4 weeks’ electrochemical chloride treatment. For the specimens, entire efficiency of dechloride lies between 60%~80%, while the efficiency of chloride near the rebar is between 70%~90%. It is obvious that the dechloride efficiency of latter is higher than the former one.

![Fig.6 Influence of the potential on the total efficiency of the chloride extraction](image1)

![Fig.7 Influence of the potential on the efficiency of the chloride extraction close to the steel bar](image2)

For different water-cement ratio specimens, the lager water-cement ratio, the better efficiency of dechloride with the same parameter is. For the specimens with ratio of W/C 0.32 and 0.38, the specimens’ entire efficiency of dechloride increase by 10% under the 20V, 40V, 60V voltage condition respectively. But for the specimens with ratio of W/C 0.45, the efficiency of specimens’ entire dechloride will increase by 13% under the voltage of 40V than the voltage of 20V, while at the 60V voltage, the efficiency just increases by 1% than the voltage of 40V. According to this, for the concrete which has high water-cement ratio, the eject resistance of chloride in specimens is small. It can fulfill the requirement to dechloride at the 40V voltage. In practical engineering, it’s unnecessary to achieve high ratio of ejectiont by using higher voltage 60V. If it is necessary to achieve high efficiency of chloride ejectment, the duration of dechloride can be increased.

As shown in figure 7, for the specimens that have high water-cement ratio (W/C=0.45), the efficiency of dechloride of the concrete near the steel is 78%, 87%, 91% under the voltage of 20V, 40V, 60V respectively with the later increase approximately by 10 percentage. But for the lower water-cement ratio specimens (W/C=0.32), the efficiency of dechloride under 40V and 20 V voltage are 86% and 72% respectively with the former increases by 14 percentage, while the efficiency under 60V voltage is almost the same as the efficiency under 60V voltage. Although the voltage is higher, the efficiency of dechloride increases little. According to these experiments, we suggest that in practical engineering for high water-cement ratio specimens, based on practical situation, 40V voltage is utilized at the beginning, and transfer to 20V voltage later. For small water-cement ratio specimens, we suggest not to use the 60V voltage through all, 40V voltage should be considered. And also later it can be transferred into 20V voltage.

Compare the amount of pre-mix salt, chloride content distribution of concrete after dechloride and the content of chloride ion in the electrolyte solution, we can make a conclusion that during the electrochemical chloride extraction process, some parts of chloride ion move out from internal layer to external layer, some parts move to electrolyte solution, and a little of them volatilize into air as chlorine.
4 Conclusions

After electrochemical chloride extraction, the residual chloride ions content in concrete shows increasing trend from inside to outside of the reinforced interface, with the least at internal layer and the most at external layer. There are 2-3.5 times differences between internal layer and external layer. And the difference between the internal layer and external layer increases with the increase of the chloride extraction voltage.

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