The Effect of the Realkalisation on the Corroded Reinforcing Bar

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Abstract This work is aimed at answering the question that whether the realkalisation as a rehabilitation method is effective on the corroded reinforced concrete structure or not. To this aim, the behaviour in a sodium carbonated solution whose concentration is 0.5 mol/L of reinforcing bars from an reinforced concrete structure that failed through carbonation after 70 years of service life is examined. The results show the electrochemical reaction on the rebar is closely related with the surface state of reinforcing bar electrode. During the electrochemical realkalisation treatment, the reduction of ferric oxide or ferrous oxide formed on the surface of reinforcing bar will occur in company with the producing of H_2; The realkalisation treatment not only resumes the alkalescence of the carbonated concrete , but also rehabilitates the corroded reinforcing bar by reducing the rust to iron. The electrochemical realkalisation treatment is a rehabilitation method and has a repairing effect on some extent of corroded reinforcing bar.

Keywords: Carbonated concrete, realkalisation, corroded reinforcing bar

Introduction

The carbonation of concrete is a well known phenomenon which can lead to the deterioration of reinforced concrete. The main cause of deterioration of carbonated concrete is the corrosion of the reinforced steel due to the decline of pH value of pore solution. The electrochemical realkalisation (ERA) is a method that the treatment applies the continuous current between the rebar and an auxiliary external electrode with the aim of restoring the alkalinity of the concrete. It is a nondestructive method of repair. Since the ERA was proposed, the research was concentrated on restoring the alkaline environment of reinforced steel. That is to say, the main purpose of ERA treatment is to raise the pH value of pore solution in carbonated concrete. Many works have been done on the ERA effect, such as electroomostic flux (Castellote et al. 2006) and material structure (Koleva et al. 2007) and electrochemical reaction (Bertolini et al. 2008). All these works seem to make the ERA technology tend to be perfect. However, few work pay the attention to the application scope of ERA. Gonzalez (Gonzalez et al. 2000)found that the rusty reinforced steel in carbonated concrete can not be repassivated after ERA treatment and got a conclusion that the ERA is only suitable to the carbonated concrete that the carbonation doesn't reach to the interface between the reinforced steel and concrete and the reinforced steel has not corroded yet. Meanwhile, few work pay attentions to the electrochemical reaction on the rusty reinforced steel. During ERA process, the electrochemical reaction on the rusty rebar may be not only the electrolysis of water; The repassivation of rebar is not only be decided to the pH value, but the surface state of rebar may also play an important role on the repassivation.

In this work, the electrochemical reaction on rust reinforced steel is investigated, and the surface statue of rust reinforced steel after ERA is analyzed, then the application scope of ERA is discussed.

Experimental

The rebars used in the simulated experiment are the rebar whose diameter is 12mm and the rusty rebar got from an old heat treatment workshop built in 1950's. In the realkalization simulated test, the

copper wire was connected with rebar as a conductor and exposed area covered with epoxy resin was $5cm^2$.

The schematic diagram for realkalization simulated test is Fig. 1. Test solution was 0.5mol/L Na_2CO_3 solution solution. Solution was bubbled with nitrogen to remove dissolved oxygen, ruling out the possibility of oxygen reduction. Current density was $5A/m^2$, and the realkalization time was 21 days. The hydrogen was collected using a flimsy rubber bag.

Electrochemical measurements were carried out by using the potentiostat (EG&G273) and related analysis software (USA PAR Company). Cyclic voltammetry scan rate was 10mV/s, and 1mV/s for polarization curve measurements. All electrode potential was relative to saturated calomel electrode (SCE).

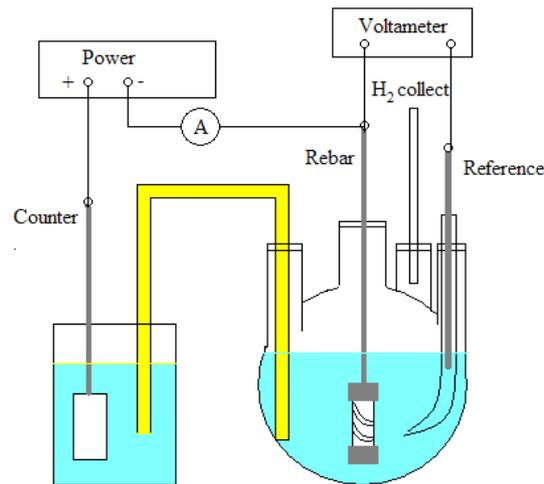*Figure 1: The schematic diagram for realkalization simulated test*

Results and Discussion

The Volume of H_2 Evolution. Fig. 2 is the volume of H_2 evolution from different rebar electrode during simulated ERA test. To the rust-free rebar, the volume of H_2 is close to the calculated volume presumed that all electric quantity was used for electrolysis of water. However, the volume of H_2 evolution which from rust rebar at same electric quantity though the electrode is less than that of calculated volume, that is to say, there are not all electric quantity used for water electrolysis.

Comparing with the rust free rebar, the volume of H_2 on rusty rebar was less than that on rust free rebar at same electric quantity (in Fig. 2). The dissolved oxygen reduction was rule out by babbling N_2, so only the rustiness reduction might take place on the rust rebar to consume the remaining electric quantity. The decrease of the ratio of $V_{H2, evolution}/V_{H2, calculated}$ with the increase of passed electric quantity means that the react rate of reduction of rustiness gradually increased during ERA treatment.
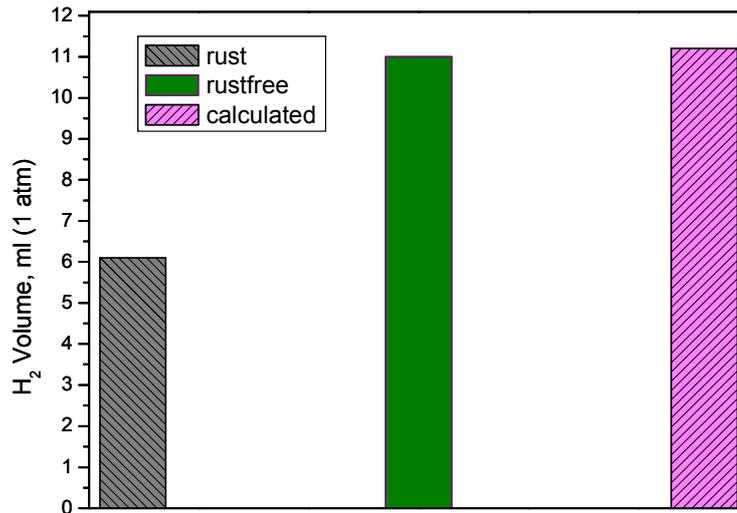
Figure 2: the volume of H_2 evolving from rebar electrode with and without rust through same coulomb in 0.5mol/L Na_2CO_3 solution for 5h (by calculated volume is meant that all coulomb were used for the H_2 evolving), current: $5A/m^2$

The Rlectrode Teaction on the Rebar Furing ERA. In alkaline environment, there were many investigations on the electrochemical transformation between Fe and its oxides (Chen and Cahan 1982, Niu 1990, Sato and Kudo 1971). All researches show that these changes have fairly reversibility and the property has applied to the second batteries, such as Fe-Ni cell (Souza et al. 2004). Fig. 3 is the cyclic voltammetry curve of rust rebar and rustfree rebar in 0.5 mol/L Na_2CO_3 solution. From the peak potential of cyclic voltammogram in Fig. 3, there are two pairs of redox peak which may correspond to $Fe(OH)_2/Fe$ and $Fe(OH)_3/Fe(OH)_2$:

$$Fe + 2OH^- \Leftrightarrow Fe(OH)_2 + 2e \qquad E^0 = -0.877V \tag{1}$$

$$Fe(OH)_2 + OH^- \Leftrightarrow Fe(OH)_3 + e \qquad E^0 = -0.56V \tag{2}$$

During the cathodic process, there are the reduction reaction of oxide (E=-500mV~-800mV) and the hydrogen evolution reaction (E=-1.221mV) on the surface of steel. And the stable potential is among the them when the cathodic current passes the electrode. During the reduction process, the reduction of Fe (III) oxide happened firstly, and Fe_3O_4 is formed by Fe (III) oxide and Fe (II) oxide reduced; In the following reactions, the process that the Fe (II) oxides are reduced to the iron may be highly in homogeneous, the iron reduced extends the oxide layer with the mode of crystallite and makes the structure of the oxide of electrode complicated, and the valence of the oxide gradually decreases with the further reduction. Finally the reduction of the oxide on the surface of the electrode is completed by the hydrogen evolution reaction and the reduction reaction.

There are two mode for reduction of iron oxide. One is dissolution-deposition mode, $[Fe(OH)_n]^{2-n}$ species that Fe(II) oxide complex with OH^- in alkaline solution was reduced and deposit to form the metallic iron; another is proton exchange mode, when the oxide on the electrode accept electron from electrode, the proton enter into the crystallites of oxide and form OH^- to keep electroneutrality and then transform to H_2O when the Fe(II) was reduced to Fe^0.

The iron crystallite was formed and a lot of empty space appeared around iron grains meaning that the reduction obeys the dissolution-deposition mode, this correspond the CV curve (Fig. 3(b)). While the reduction of Fe(III) to Fe(II) may obey the proton exchange due to the lower dissolvability of $Fe(OH)_3$ or Fe_3O_4 in alkaline solution, then the $Fe(OH)_2$ transform to $[Fe(OH)_n]^{2-n}$ and was reduced to Fe^0 by dissolution-deposition mode.

Furthermore, it should be pointed out that not all rust could be reduced because that the existence of loosen of rustiness is the main cause for low electric conductivity. And more coulometry is used for the evolution of H_2.
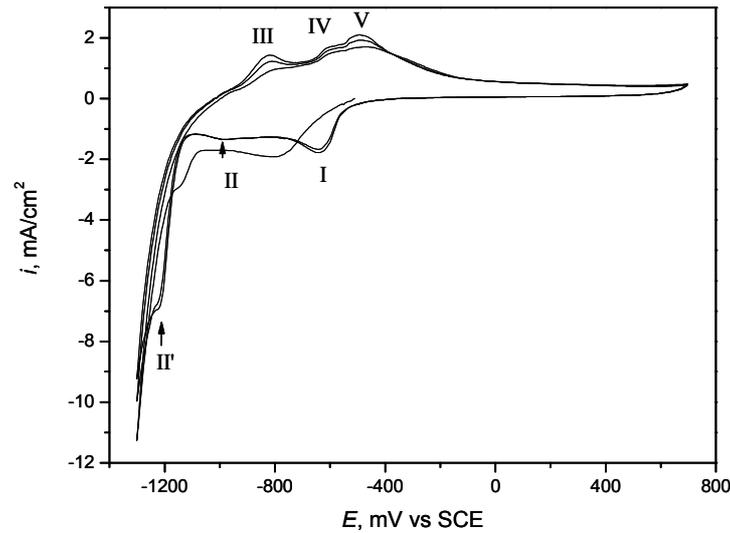
(a) rustfree rebar as electrode
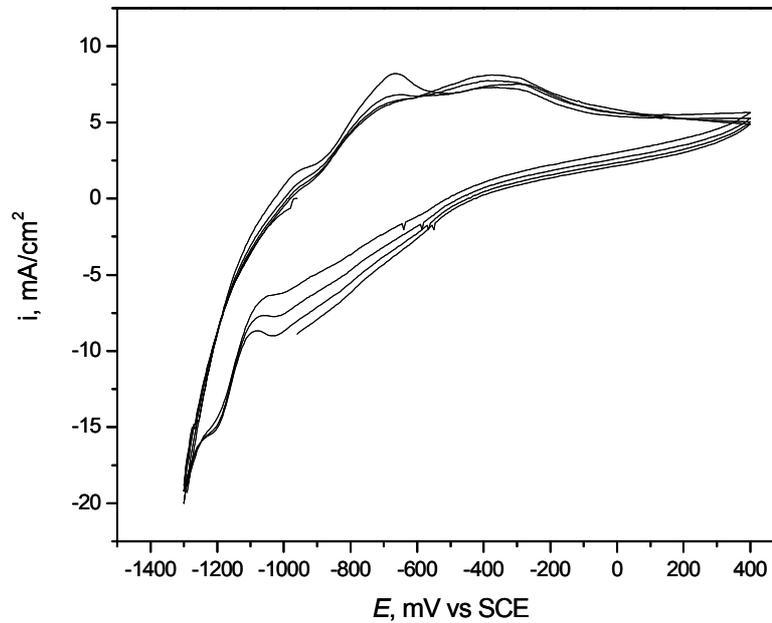
(b) rust rebar after ERT as electrode

Figure 3: the CV curve of the rebar in 1mol/L Na_2CO_3 solution, scan rate: 10mV/s

The Passivation of Rebar after ERA Treatment. Fig. 4 is the polarization curve of the rebar at different status. For rust-free rebar, like other reports, the OCP would keep a negative value in range -0.7~-0.6V and the corrosion current is very small; after ERA treatment, the rebar would be passivated. Meanwhile, for rust rebar, the OCP would keep a negative value in range -0.9~-0.8V and the corrosion current is larger than that of rust free rebar; After ERA treatment, the OCP and the corrosion current of rust rebar is larger than before ERA treatment.
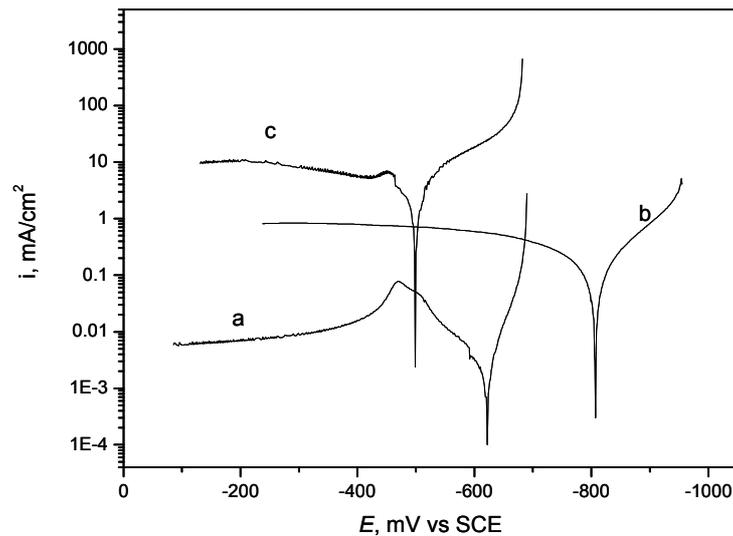
(a) rustfree rebar (b) rust rebar (c) rust rebar after ERT

Figure 4: the polarization curve of the rebar at different status (solution, 0.5mol/L Na₂CO₃ solution)

Conclusion

After ERA treatment, the passivation of rebar in carbonated concrete was decided by two conditions. One is the alkaline environment of concrete, according to Pourbaix gram of Fe-H_2O system, when pH>10, the rebar might be in passive state; another is the surface status of rebar, for the rebar with smooth surface, the rebar could react with depolarizer (such as dissolved O_2 in solution) and the reaction product enough to form a compact passive film to protect rebar substrate duo to its less specific surface area. While, for a rust rebar, it has a large specific surface area owing to its coarse surface caused by corrosion, at same condition, the reaction product as stated above on the rebar surface can not form a compact film. For deeply carbonated concrete, the rebar has corroded in low pH environment and form a rust layer on rebar. Although the rust could be reduced to metallic iron, the Fe crystal were fine and dispersive, not a compact deposit due to the low concentration of $[Fe(OH)_n]^{2-n}$ and could not be in passive state. Gonzalez's group also has same result and concludes that the ERA could not apply to the deeply carbonated concrete structure (Miranda 2006).

Acknowledgment

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