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EFFECTS OF THE CATHODIC CURRENT ON ALKALI-SILICA AGGREGATE REACTION

Jiang-Jhy Chang, Weichung Yeh, and Cheng-Chin Chang

Key words: alkali-silica aggregate reaction, crack opening width, chemical titration.

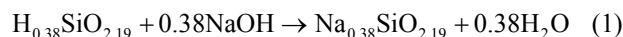
ABSTRACT

In this study, we investigated whether the cathodic current accelerates the alkali-silica aggregate reaction. Variables considered were the water/cement (w/c) ratio, initial alkali content, and cathodic current. The crack initiation time, crack mouth opening history, and microhardness values were monitored to examine the effect of the cathodic current on crack initiation and propagation due to the alkali-silica aggregate reaction. In addition, chemical titration was performed to determine the amount of accumulated sodium and potassium ions to support our viewpoints. The results showed that the crack initiation time shortened with an increase in the initial alkali content, w/c ratio, and/or cathodic current density. Furthermore, the crack opening rate increased in the same manner. Microhardness values indicated that the Calcium-Silicate-Hydrate (CSH) gel near the rebar (cathode) had the strongest softening effect. Moreover, the microhardness value for the concrete near the rebar was related to the influencing parameter, ϕ , which is defined as the product of the cathodic current density and polarization time. Chemical titration proved that the total amount of accumulated potassium and sodium ions increased with an increase in ϕ . The relation between ϕ and the crack initiation time was investigated when the w/c ratio and the initial alkali content were maintained as constants. The crack initiation time shortened with an increase in ϕ . In addition, the crack growth rate increased with an increase in ϕ . The microhardness value decreased linearly with an increase in ϕ . Thus, the cathodic protection on the reinforced concrete (RC) structure should be carefully applied, particularly for concrete with high potential of the alkali-silica aggregate reaction.

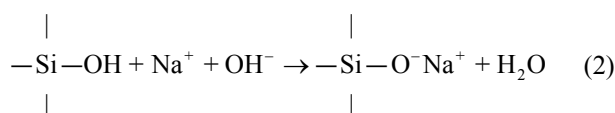
I. INTRODUCTION

The alkali-silica reaction was first demonstrated by Stanton

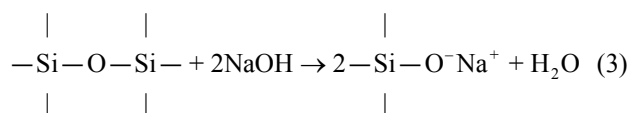
(1940). Currently, this reaction is known as the chemical reaction between alkali ions (Na^+ and K^+) provided from cement paste and the quasi-stable silica from potentially reactive aggregates. Such a reaction yields an alkali-silica gel, which expands on absorbing water. This expansion produces pressure such that cracks in concrete may appear. The alkali-silica reaction is written as follows:



Many studies have proposed the possible mechanisms for the alkali-silica reaction. Among them, two explanations, one from Powers and Steinour (1955) and another from Chatterji (1989), are most popular to the scientific community. Powers and Steinour claimed that a thin film of silanol groups exists on the interface between the reactive silica particles and water molecules such that the hydration of silica particles yields a surface layer containing OH^- ions. When the reactive silica particles are exposed to a low concentration of hydroxide alkaline solution, -silanol groups are neutralized- as follows:



The negative charge of Si-O- attracts more Na^+ , K^+ , and Ca^{2+} to migrate toward the gel to reach the electrical equilibrium, at which anions are provided from cement. As the concentration of the hydroxide alkaline solution increases, the following reaction occurs:



Several crucial points were presented in their proposed mechanism:

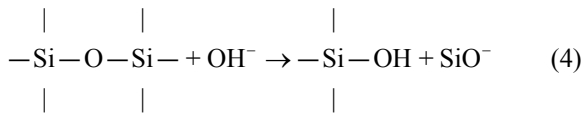
- (1) The amount of anions penetrating into the thin film is controlled by the concentration of the alkaline solution outside the film. In addition, only Na^+ and K^+ induce the

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expansion of alkali-silica compounds.

- (2) To reduce the alkali-silica reaction, the concentration of the alkaline solution outside the film can be reduced. Therefore, pozzolian materials can inhibit the alkali-silica reaction (Thomas and Innis, 1998).

The mechanism proposed by Chatterji is summarized as follows. When $\text{pH} \geq 7$, OH^- ions penetrate into the silica particles. The amount of penetrating OH^- ions depends on the solution pH and anion concentration. If the pH and anion concentration remain as constants, the absorption of OH^- ions decreases with an increase in the anion radius. The OH^- ions then destroy the Si-O-Si bonding as shown in the following reaction:



As shown, the reaction releases some silica. The amount of the released silica depends on the Ca^{2+} concentration in the environment. If the Ca^{2+} concentration is high, a low amount of silica is released. When the concentration of the material that penetrates into the silica particles, such as Na^+ , Ca^{2+} , OH^- , and water, is greater than the concentration of silica released, expansion occurs. The crucial point of the Chatterji mechanism is that the alkali-silica reaction can occur when OH^- and alkali ions exist. The existence of alkali hydroxide is not necessary. For example, $\text{NaCl} + \text{Ca}(\text{OH})_2$ can stimulate the alkali-silica reaction.

The alkali-silica reaction will reduce the mechanical properties of concrete. The dynamic elastic modulus is highly sensitive to the alkali-silica reaction such that it can be used to detect the initiation of the reaction (Swamy and Al-Asali, 1986). Several methods have been proposed to inhibit the alkali-silica reaction, such as water-proof coating, adopting $\text{Li}(\text{OH})$ (Lumeley, 1997), and adopting pozzolian materials (Thomas and Innis, 1998).

Cathodic current has been developed for realkalization (Mietz, 1995; Yeih and Chang, 2005), desalination (Ihekwa et al., 1996; Chang, 2003), and cathodic protection (Pedferri, 1996). However, the use of the cathodic current has a few drawbacks, including bond degradation (Chang, 2002), hydrogen embrittlement (Chang et al., 1997), degradation of mechanical strength (Ihekwa and Hope, 1996), and acceleration of the alkali-silica reaction (Ali and Rasheeduzzafar, 1993).

Shehata and Thomas (2000) studied the effect of the addition of fly ash to inhibit the alkali-silica aggregate reaction. Diamond (1999) proposed the use of LiNO_3 to prohibit the alkali-silica reaction. He claimed that the presence of lithium hydroxide increases the OH^- ion concentration, which is known to inhibit the alkali-silica aggregate reaction, whereas the use of lithium nitrate can avoid this drawback. Ramlochan et al. (2000) introduced high-reactivity metakaolin to control

Table 1. The grade of Pyrex glass.

sieve size passing through	sieve size retained	weight percentage (%)
#8 (2.36 mm)	#16 (1.18 mm)	10
#16 (1.18 mm)	#30 (600 μm)	40
#30 (600 μm)	#50 (300 μm)	40
#50 (300 μm)	#100 (150 μm)	10
Total		100

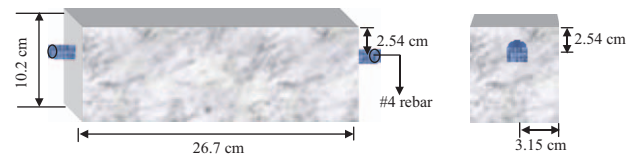


Fig. 1. The mortar specimen configuration.

the expansion caused by the alkali-silica reaction. Shehata and Thomas (2002) used ternary blends containing silica fume (SF) and fly ash to suppress the expansion caused by the alkali-silica reaction in concrete. They found that pastes containing SF yield pore solutions of high alkalinity at ages beyond 28 days, and pastes containing ternary blends maintain the low alkalinity of the pore solution throughout the testing period (3 years). Bažant and Steffens (2000) proposed a mathematical model to describe the chemical kinetics of the alkali-silica reaction. Rodrigues et al. (1999) measured the surface charge density of silica and studied its effect on expansion pressure. Bleszynski et al. (1998) reported that fly ash can effectively suppress the expansion caused by the alkali-silica reaction.

Although a possible acceleration of the alkali-silica reaction caused by the cathodic current has been investigated by Ali and Rasheeduzzafar (1993), to our knowledge, an integrated study on such a phenomenon has not been conducted. We study the influence of the cathodic current on the alkali-silica reaction.

II. EXPERIMENTAL

1. Specimens

The size of the mortar specimens was 267 mm \times 102 mm \times 63 mm, and a steel rebar with the nominal diameter of 12 mm (#4 rebar) was embedded as shown in Fig. 1. The mortar was prepared using type I Portland cement, and the water/aggregate ratio was 1. The water/cement ratios were 0.3, 0.4, 0.5, and 0.6. To study the effect of the initial alkali content, NaOH solution was used to adjust the initial alkali (Na_2O) content to 0.48%, 1.00%, 1.50%, and 2.00% by the weight of cement, where 0.48% is the minimum alkali content that is provided by cement. The aggregates used were Pyrex glasses, which simulate the potentially reactive aggregates. The grade of aggregates is listed in Table 1. Specimens were cured under the standard curing condition for 28 days. After curing, they

were connected to the DC power supply with the rebar acting as the cathode and the titanium mesh acting as the anode. The electrolyte was a 3.5% NaCl solution, which simulates the marine environment. Cathodic current densities used were 0, 400, 800, and 1200 $\mu\text{A}/\text{cm}^2$.

2. Experiments Conducted

After apply the cathodic current to the specimens, the first sign of the initial surface crack was recorded. The definition of an initial crack depends on the minimum crack width that can be measured by the apparatus (0.1 mm for the crack displacement measurement apparatus in this study). The time required for the appearance of the first signs of crack under various conditions were recorded. After initial cracks were observed, the crack mouth opening history was recorded using the same apparatus. The crack mouth opening displacement is expected to increase with an increase in the amount of expansive gel formed by the alkali-silica reaction.

The microhardness test was performed to examine the changes in mechanical properties during the acceleration of the alkali-silica aggregate reaction. For this experiment, an awl with specific weight falls from a height and has an impact on the surface of the specimens. A stamp of the awl is then formed on the specimen surface. We measured the depth of the stamp and used it to represent the microhardness of the surface.

To confirm that the cathodic current attracts more alkali ions to migrate toward the cathode such that the alkali-silica reaction accelerates, chemical titration was conducted to determine the amount of potassium and sodium ions. In this experiment, we used computer-controlled titration, and an accurate result was achieved.

III. RESULTS

1. First Sign of Initial Cracks

The influence of the initial alkali content on the first sign of cracking is illustrated in Figs. 2(a) to 2(c). As seen, the first sign of initial cracks appeared earlier for specimens with a high initial alkali content. In addition, for the same initial alkali content, a high cathodic current density shortened the duration for observing the first sign of the initial crack. Specimens with a high water/cement ratio had a shorter duration for the appearance of the first sign of the initial crack. The image of the surface crack due to the acceleration of the alkali-silica aggregate reaction is illustrated in Fig. 3. The main crack propagated along the direction of the rebar, which is different from the map cracks that usually appear when the alkali-silica aggregate reaction occurs. This can be attributed to two reasons: (1) the alkali-silica aggregate reaction for cathodically protected specimens occur locally, that is, near the rebar and (2) the local volumetric expansion of the gel causes cracks to propagate along the direction of the rebar, which is similar to the case of cracks caused by corrosion products.

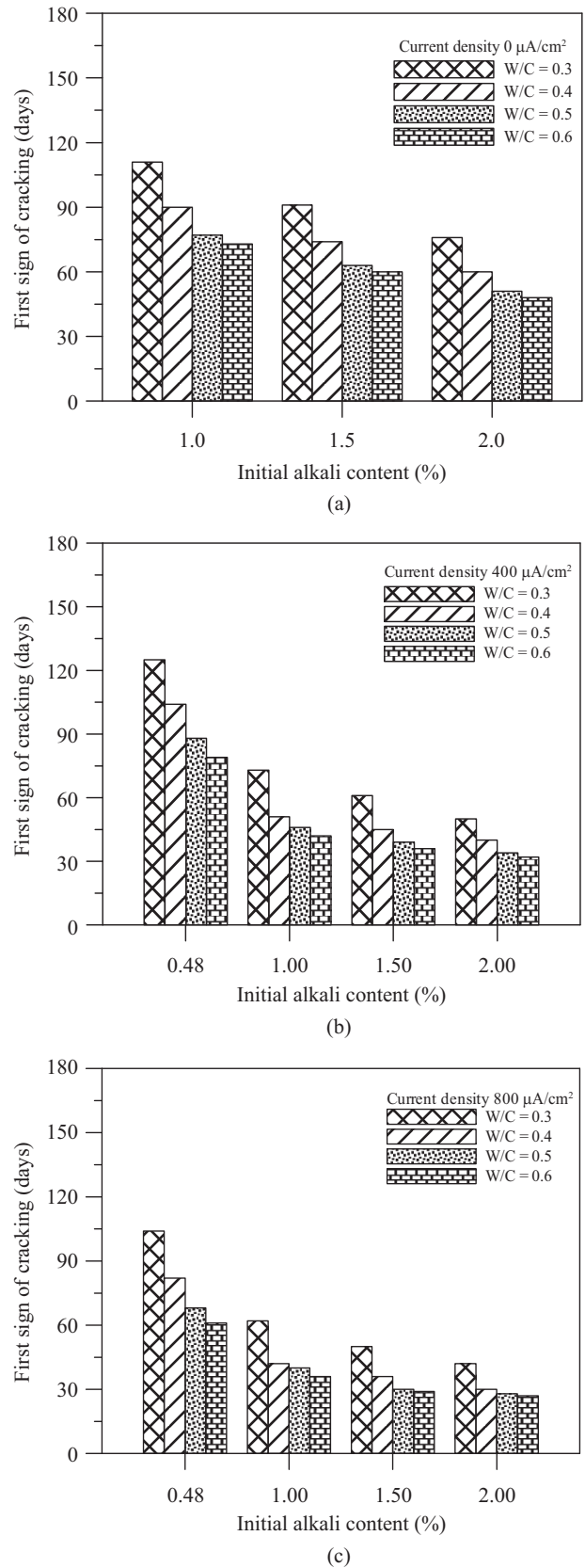


Fig. 2. The influence of initial alkali content on the first sign of cracking for various cathodic current densities: (a) 0 $\mu\text{A}/\text{cm}^2$; (b) 400 $\mu\text{A}/\text{cm}^2$; (c) 800 $\mu\text{A}/\text{cm}^2$.



Fig. 3. The photo of the surface crack induced by the alkali-silica aggregate reaction.

2. Crack Growth

Crack growth was monitored once the first signs of cracks were observed. The influence of the initial alkali content on the crack growth is illustrated in Fig. 4. As seen, after the initial crack was formed (crack width, 0.1 mm), the crack width opened faster when the initial alkali content was high. Thus, a high initial alkali content causes the alkali-silica aggregate reaction to be more dangerous when the reinforced concrete is protected by the cathodic current. The influence of the water/cement ratio on the crack growth is illustrated in Fig. 5. As shown, concrete with a high water/cement ratio had a faster crack opening rate. This can be attributed to two reasons: (1) concrete with a high water/cement ratio has a loose microstructure such that the alkali ions from the environment can penetrate into the concrete and migrate toward the rebar more easily under the cathodic current conditions, resulting in a more critical alkali-silica aggregate reaction, and (2) concrete with a high water/cement ratio has low mechanical strength such that it cannot sustain stresses introduced from the crack formation. The influence of the cathodic current density on the crack growth is illustrated in Fig. 6. As shown, after the first sign of crack was observed, no substantial difference among various cathodic current densities was identified within the first 10 days. However, after 10 days, a high cathodic current density caused a high crack opening as expected. The retard effects may be explained as follows. The first sign of crack can be justified as the effect of initial alkali content that existed in the concrete. When the cathodic current was applied, the initial alkali ions inside the concrete were attracted and migrated toward the rebar, consequently resulting in the crack. In addition, the alkali ions from the environment might not reach the concrete-rebar surface yet. These extra alkali ions require some time to reach the concrete-rebar surface to produce a more critical crack such that the difference between various cathodic current densities can then be observed. After the extra alkali ions reach the interface and the crack opens, a higher cathodic current density attracts more extra alkali ions within the same duration such that the

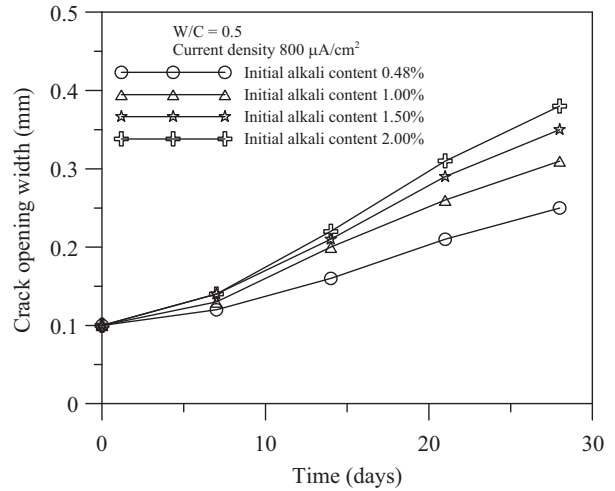


Fig. 4. The influence of initial alkali content on the crack opening width.

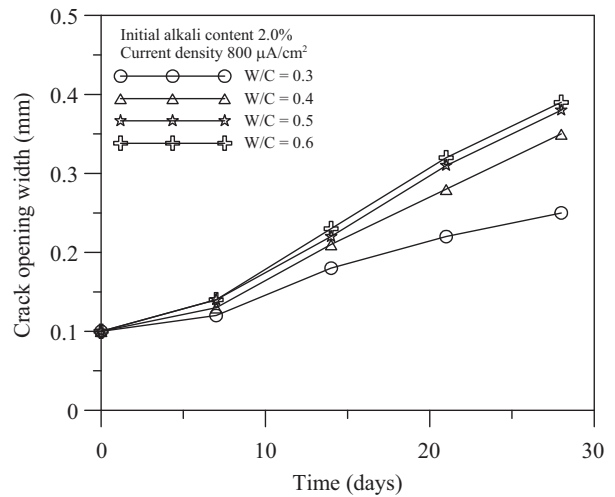


Fig. 5. The influence of w/c ratio on the crack opening width.

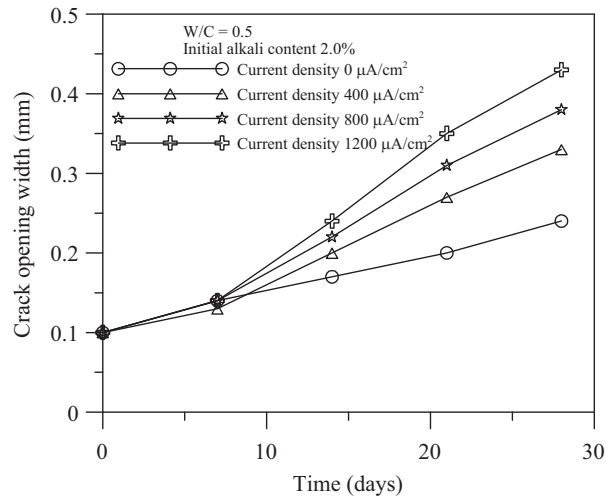


Fig. 6. The influence of cathodic current density on the crack opening width.

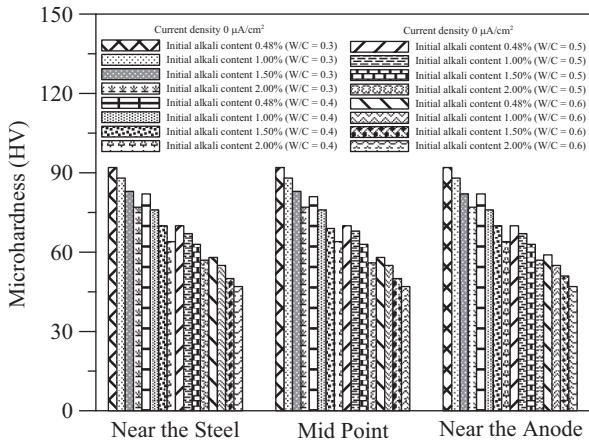


Fig. 7. Microhardness values for control specimens.

opening is more noticeable. Consequently, a larger crack opening means more free paths that allow foreign agents to penetrate into the concrete, accelerating the crack opening.

3. Microhardness

The microhardness test was performed to examine the change in the mechanical property locally. As shown in Fig. 7, the microhardness values of the concrete were uniform without the application of the cathodic current. In addition, concrete with a high initial alkali content has a low microhardness value, indicating that the alkali ions react with the CSH gel and reduce the mechanical strength of the concrete. As shown in Figs. 8(a) to 8(c), after the application of the cathodic current, the microhardness value near the cathode decreased and those at the midpoint and near the anode remained unchanged. This observation strongly suggests that the change in mechanical properties is due to the cathodic current, and this is consistent with a previous report (Powers and Steinouer, 1955). In addition, such a degradation effect became more significant when the applied cathodic current density was high. On the basis of previous studies (Ihekwa et al., 1996; Lumeley, 1997), we defined the influencing parameter ϕ as follows:

$$\phi \equiv i_c \times t_p \quad (5)$$

where i_c is the cathodic current density and t_p is the polarization time. The influencing parameter represents the total charge transferred through a unit protected surface area during a specific duration. Changes in several properties are found to be related to this influencing parameter. The changes in the microhardness value near the rebar-concrete interface are presented with respect to the influencing parameter shown in Figs. 9(a) to 9(d). The microhardness value decreases with an increase in the influencing parameter.

Diversity techniques, which are widely used for combating multipath fading effects, can be implemented in numerous ways. In this study, we used a relatively simple yet effective spatial diversity technique called the equal gain combining

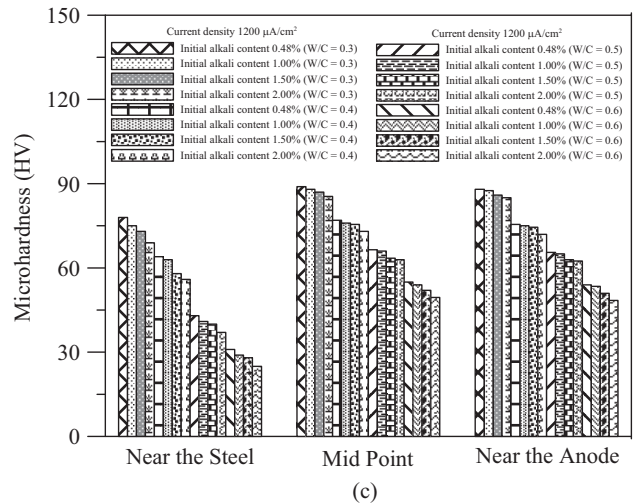
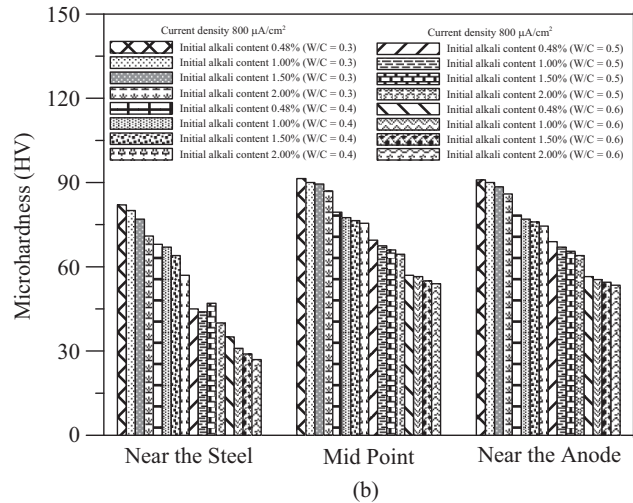
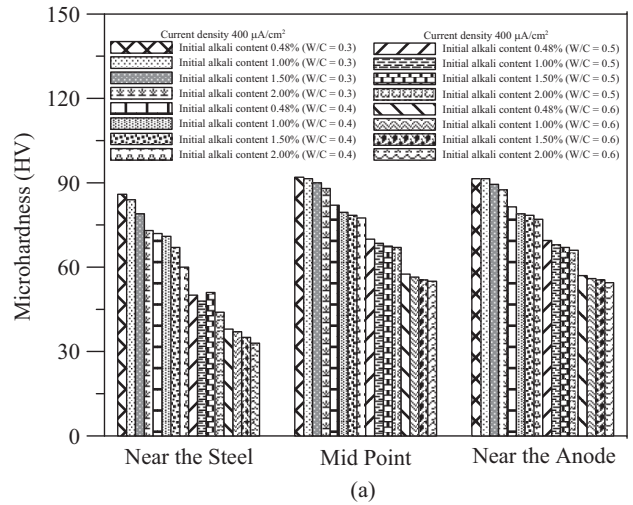


Fig. 8. Microhardness values under various cathodic current densities: (a) 400 $\mu\text{A}/\text{cm}^2$; (b) 800 $\mu\text{A}/\text{cm}^2$; (c) 1200 $\mu\text{A}/\text{cm}^2$.

(EGC) technique. The EGC technique combines the received signals from multiple hydrophones at different spatial locations to form a signal with a high signal-to-noise ratio (SNR).

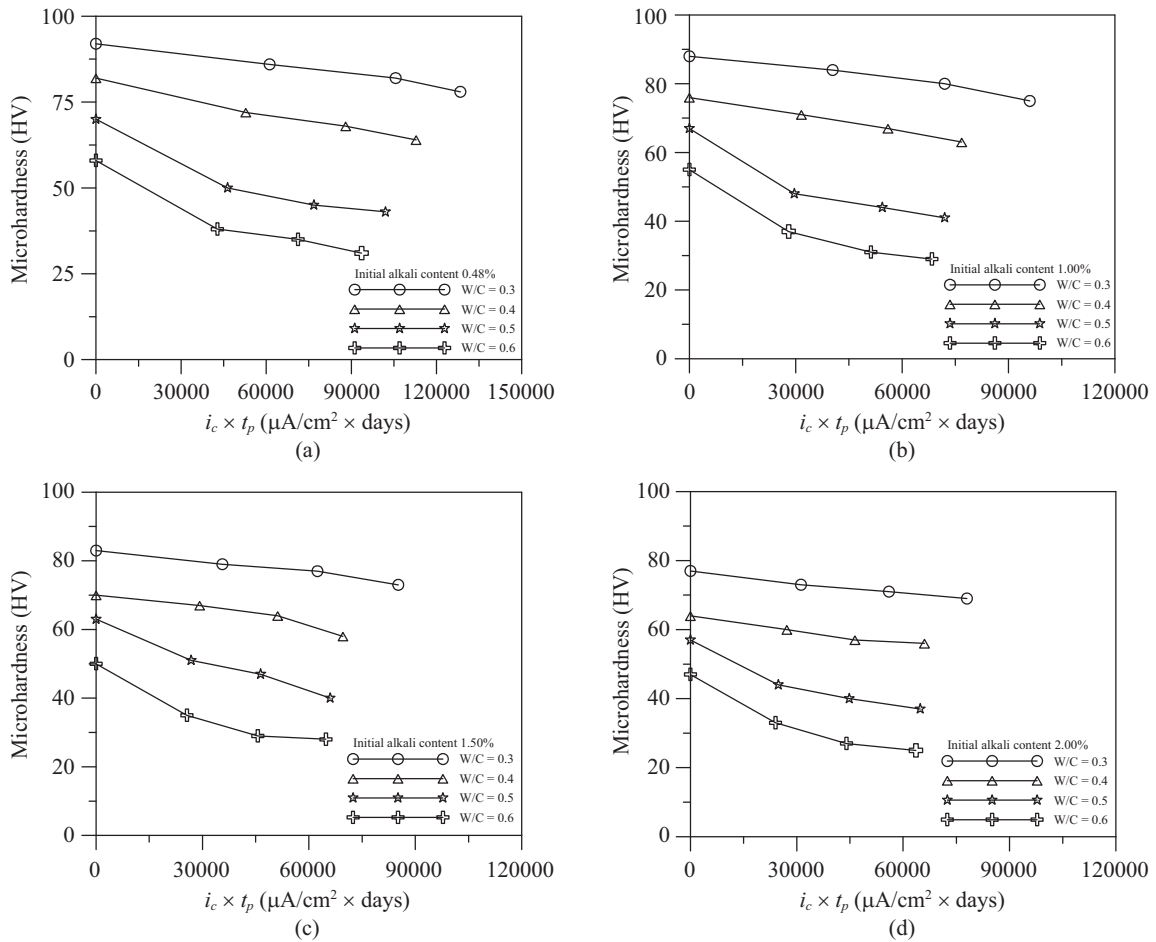


Fig. 9. The relationship between the influence parameter and the microhardness values nearby the rebar for various initial alkali contents: (a) 0.48%; (b) 1.0%; (c) 1.5%; (d) 2%.

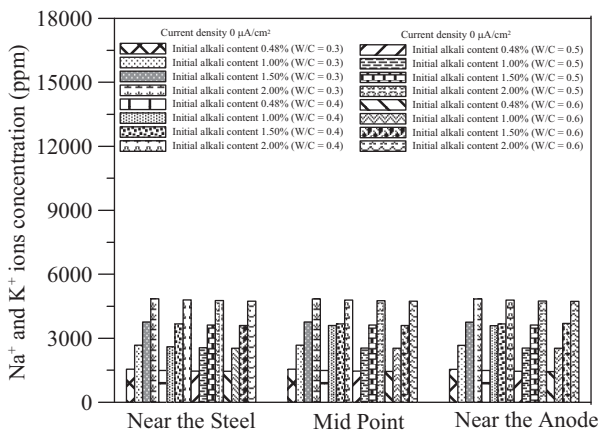


Fig. 10. The initial potassium and sodium ions for the control specimen.

4. Chemical Titration

Chemical titration was performed for determining the amount of potassium and sodium ions. In Fig. 10, the alkali content remained uniformly distributed without the application of the cathodic current. After applying the cathodic current, the alkali

ion content near the rebar increased dramatically as shown in Figs. 11(a) to 11(c). The relationship between the alkali ion content and influencing parameter is illustrated in Fig. 12. The linear relationship between the microhardness value and accumulated amount of potassium and sodium ions was analyzed on the basis of Figs. 9(a) to 9(d) and (12) and is shown in Fig. 13.

To test the effectiveness of the proposed transceiver in a fading environment, we conducted a simulation by using a five-ray Rayleigh fading channel model (Chang et al., 1997). In this simulation, we used a DS/SS QPSK modulation with a 7-bit PN code. A (15, 11) BCH error correction code was employed. The carrier frequency was 24 kHz, the sampling rate was 384 kHz, the symbol rate was 1985 symbols/sec, and the SNR was set at 9 dB. The simulation result is shown in Table 1. In addition, the result obtained using two receivers with the EGC technique is shown in Table 1. The EGC technique improved the BER performance.

IV. CONCLUSIONS

The alkali-silica aggregate reaction accelerates when the

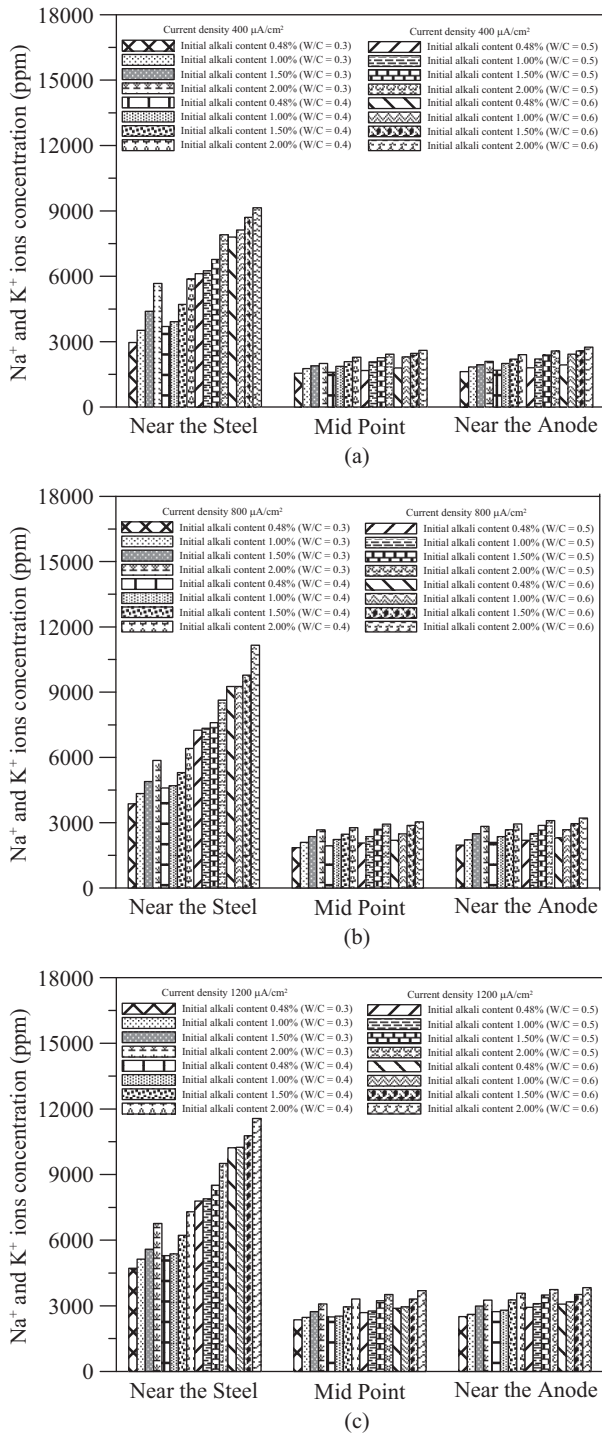


Fig. 11. The accumulate potassium and sodium ions under various cathodic current densities: (a) 400 $\mu\text{A}/\text{cm}^2$; (b) 800 $\mu\text{A}/\text{cm}^2$; (c) 1200 $\mu\text{A}/\text{cm}^2$.

cathodic current is applied. The crack growth rate depends on the initial alkali content, water/cement ratio, and applied cathodic current density. The changes in the microhardness value indicate that the mechanical change mainly occurs for concrete near the rebar. As verified by chemical titration, the

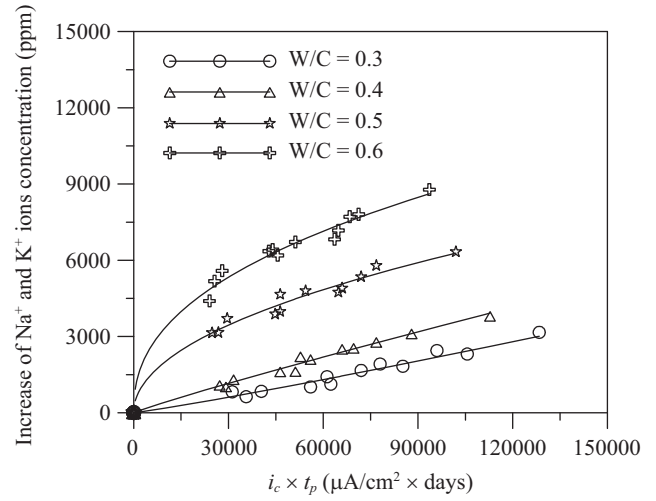


Fig. 12. The relationship between the influence parameter and the accumulated potassium and sodium ions.

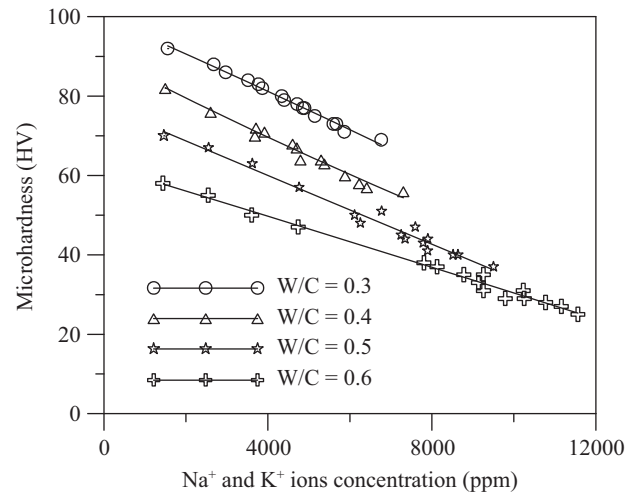


Fig. 13. The relationship between the microhardness values and the accumulated potassium and sodium ions.

changes in the mechanical properties are strongly related to the accumulated alkali ion content, which strongly relates to the influencing parameter, that is, the cathodic current density and polarization period. Thus, the application of the cathodic current to concrete with a high risk of the alkali-silica aggregate reaction may result in the acceleration of the alkali silica reaction, and such application should be carefully designed and conducted to avoid possible expansion due to the alkali-silica reaction.

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