

Influence of the C-S-H Amount on $[\text{Cl}^-]/[\text{OH}^-]$ Ratio of Simulated Concrete SPS and the Corrosion Susceptibility of Steel

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Abstract: Two kinds of simulated concrete pore solutions (SPSs) were treated with different amounts of synthetic calcium silicate hydrate (C-S-H). The variation of the $[\text{Cl}^-]/[\text{OH}^-]$ ratio in SPS was measured and the corrosion susceptibility of carbon steel in the SPS was investigated with potentiodynamic polarization, EIS and weight loss tests. The experimental results showed that for the SPS at pH 12.5, as the amount of C-S-H increases, the $[\text{Cl}^-]/[\text{OH}^-]$ ratio increases thereby causing an increase in the corrosion susceptibility of the steel. While for the SPS at pH 9.7, with increasing C-S-H amount, the drop amplitudes of both $[\text{Cl}^-]/[\text{OH}^-]$ ratio and steel corrosion rate first decrease and then increase, and a 3% C-S-H addition shows the best inhibition effect. XPS results demonstrate that after C-S-H treating in pH 12.5 SPS the $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ ratio in the film on steel surface is reduced while in pH 9.7 SPS the $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ ratio is increased. The different effects of the C-S-H amount on the two SPSs and the steel corrosion behavior result from the influences of C-S-H on the SPS pH, which is related to the composition of the SPS.

Key words: C-S-H; concrete SPS; $[\text{Cl}^-]/[\text{OH}^-]$; corrosion; carbon steel

1 Introduction

Generally, reinforcing steel is well protected against corrosion by a passive oxide film within high alkaline environment of concrete. However, the steel will suffer severe corrosion problems when the reinforced concrete structure is exposed to chloride contaminated environments and/or when the concrete cover is carbonated. It was reported that above a $[\text{Cl}^-]/[\text{OH}^-]$ threshold value, the passive film on steel surface will be broken down^[1,2]. Therefore, to reduce the chlorides content and enhance the pH value of the concrete environment would be beneficial to prevent the corrosion of steel and extend the life of reinforced concrete structure.

Calcium silicate hydrate (C-S-H) is the main hydration product and primary binding phase in Portland cement. Its composition and structure are

very complex and vary with the hydration time and the environmental conditions^[3,4]. Usually, the Ca/Si ratio can be used to characterize the chemical composition of C-S-H^[4]. As a porous substance, C-S-H has a strong adsorption performance and thus can adsorb chloride ions effectively^[5,6]. The adsorption ability is influenced by many factors including chloride concentration, Ca/Si ratio, concrete carbonation and hydroxyl concentration in the environment^[5]. Meanwhile, C-S-H can also adsorb alkali ions such as Na^+ or K^+ in the environmental solution. One important reason is that there are acidic silanol Si-OH groups in C-S-H structure, so the alkaline cations would be able to substitute a part of the protons on the C-S-H surface^[7-9]. In addition, silicate anions are not integrated structure chains, there are non-bridging oxygens on the broken chains, which have negative charges, thereby have an affinity for cations^[8]. So, K^+ and Na^+ cations could be bound to C-S-H by a compensation of the negative surface charge of C-S-H^[9].

In our previous work^[10], five kinds of simulated concrete SPSs were treated with synthetic C-S-H (3wt%) and the corrosion behaviors of carbon steel in solutions were studied. It was found that in solutions at pH above 11, the corrosion of steel was improved,

while in solutions at pH below 11 the corrosion was inhibited. The reason was that C-S-H treatment could reduce the pH value of the former solutions and increase the pH value of the latter. In this paper, the research was focused on the influence of C-S-H amount on the comprehensive impacts of C-S-H on chloride and hydroxyl ions of two kinds of SPSs, which represent the alkaline and carbonated concrete situations, respectively. The variation of the corrosion susceptibility of carbon steel was also investigated and the related mechanism was discussed.

2 Experimental

2.1 Steel material and preparation of C-S-H

The study material was Q235 carbon steel with the chemical composition (wt%) of C 0.15, S 0.02, P 0.026, Si 0.17, Mn 0.42, and Fe bal. The size of steel specimen for electrochemical test was $\phi 1.4 \text{ cm} \times 1 \text{ cm}$. A copper wire was soldered to the end of the specimen for electrical contact. The specimen surface was abraded with emery papers up to 1000 grit, rinsed in de-ionized water and degreased with acetone, and then covered with epoxy resin leaving an area of 0.28 cm^2 exposed to the test solution. For weight loss and XPS tests the size of the steel specimens was $20 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$.

Calcium silicate hydrate (C-S-H) was prepared by $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. The details of sample preparation and experimental procedure are given in the Ref.[10]. The Ca/Si ratio was 1.5.

2.2 Preparation of simulated SPSs and test of pH value and chloride ions

The composition of the alkaline SPS (pH 12.5 SPS) was saturated $\text{Ca}(\text{OH})_2$ solution, and the composition of the carbonated SPS (pH 9.7 SPS) was $0.04 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{CO}_3 + 0.03 \text{ mol} \cdot \text{L}^{-1} \text{ NaHCO}_3$ solution^[2]. 0.08 mol/L NaCl was added into each solution and then 1wt%, 3wt%, and 6wt% C-S-H was added separately. The mixture was stirred for 8 h at room temperature then filtered with a vacuum suction filter. After the process, the pH value was measured using a pH meter and the chloride content was determined by a pCl^{-1} type chloride ion selective electrode (Leici Corp).

2.3 Electrochemical test and corrosion weight lost test

Potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS) were carried out to evaluate the corrosion behavior of the steel specimen in SPSs before and after treating with

different amounts of C-S-H. Polarization curves were measured with a CS300 potentiostat (Wuhan Corrtest Instrument Co.). The potential scan rate was 0.6 mV/s and started from -300 mV minus the open circuit potential. EIS tests were performed with a Princeton PARSTAT 2273 instrument. The AC disturbance signal was 10 mV and the frequency varied from 10^5 to 10^{-2} Hz. All the tests were performed at room temperature in a glass cell with a platinum electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

The weight lost test was performed after the steel specimen immersed in SPSs before and after treating with different amounts of C-S-H. The immersion time was 168 h. Then, the steel surface was observed with an optical microscope and the corrosion rate was calculated.

3 Results and discussion

3.1 Influence of C-S-H amount on the pH and the chloride content of pH 12.5 SPS

Fig.1 shows the variations of pH values and chloride contents in the SPSs before and after C-S-H treatment. The original pH of the solution was 12.5. It can be seen that after treating with different amounts of C-S-H, the pH values decrease apparently (Fig.1(a)) and the drop amplitude increases with the rise in C-S-H amount. It is reported that^[9] the interaction between C-S-H and ions from environmental solution is related to the charge compensation on the C-S-H surface. For the C-S-H with high Ca/Si ratio (> 1.0), a part of H^+ in acidic silanol Si-OH groups can be easily replaced by Ca^{2+} ^[9]. Because the pH 12.5 SPS contains high concentration of hydroxyl ions, many OH^- ions would react with H^+ and Ca^{2+} in the C-S-H structure which would result in the pH value decrease. In addition, some Ca^{2+} cations in the SPS might be adsorbed on the non-bridging oxygen sites which have negative charges, resulting in an increased positive charge^[5] and subsequent adsorption of negative OH^- ions, leading to the decrease in OH^- content and thereby pH decrease. With more C-S-H added, more acidic silanol Si-OH groups and Ca^{2+} ions exist in the structure, which could react with more OH^- from the solution, leading to a bigger decrease in the pH value of SPS. The reason of no obvious difference in the pH drop from 3% to 6% addition might be due to a maximum binding capacity of C-S-H structure for alkaline.

Fig.1(a) also shows that the chloride concentration

in the SPS decreases remarkably after treating with different amount of C-S-H, about one tenth of the original chloride concentration. The chloride concentration in the solution with 6% C-S-H added is a little higher than that with 3% C-S-H (0.0085 and 0.007, respectively.) Yuan *et al*^[5] pointed out that the binding of chloride ion by C-S-H is very complicated. Except for the C-S-H structure and amount, chloride concentration and cations etc., it is also related to hydroxyl concentration in the environmental solution. There is a competition between hydroxyl and chloride ions during their adsorption in the interlayers of C-S-H^[11,12]. So when more C-S-H is added into the solution, more OH^- would be adsorbed, which could probably cause less Cl^- ions binding to some degree.

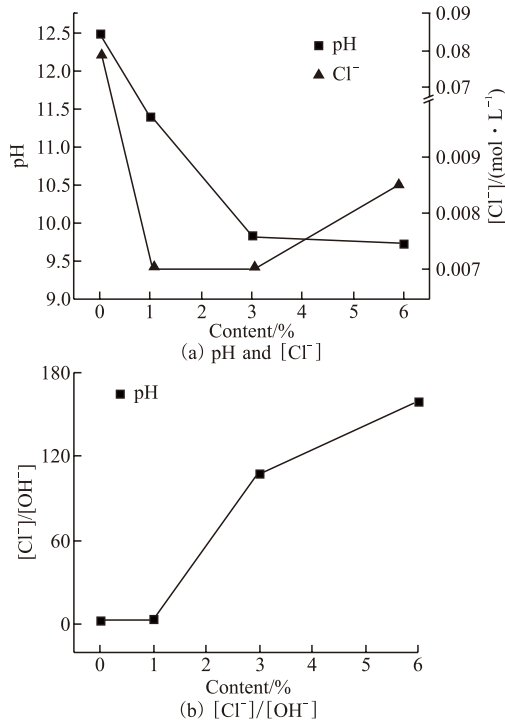


Fig.1 Influences of C-S-H amount (1%, 3%, and 6%) on pH 12.5 pore solution

The ratio of chloride to hydroxyl ions ($[Cl^-]/[OH^-]$) in SPS is an important parameter to evaluate the onset of corrosion on reinforced steel. The higher the ratio, the bigger the corrosion risk of steel by chloride ions^[1]. Generally, the pH value of the solution increases, the threshold ratio will increase^[2]. For most reinforced concretes the $[Cl^-]/[OH^-]$ threshold ratios are in the range of 0.66 to 1.4^[13]. Fig.1(b) shows the $[Cl^-]/[OH^-]$ ratio in SPS after C-S-H treating. It can be seen that before treatment, the ratio is 2.53, which is slightly above the $[Cl^-]/[OH^-]$ ratio at the threshold of corrosion. After 1% S-C-H added, the ratio slightly increased to 2.79, which indicates the improved

corrosion tendency of the steel. After adding 3% or 6% S-C-H, the $[Cl^-]/[OH^-]$ ratio increases to 108.00 or 160.14 remarkably. So, for the pH 12.5 SPS 1% C-S-H treatment has no very big influence on the corrosion risk of the steel, but 3% and 6% C-S-H causes much higher corrosion risk.

3.2 Influence of C-S-H amount on the corrosion behavior of the steel in pH 12.5 SPS

Fig.2 shows the polarization curves of the steel specimens in SPSs without or with 1%, 3%, and 6% C-S-H treating, respectively. It is shown that an extended passive region exists on the anodic polarization part for solution without C-S-H, indicating good passive behavior of the steel. After C-S-H treating, the corrosion potential shifts to negative direction and the passive region becomes narrower. With increasing C-S-H amount, the active corrosion characteristic is distinct gradually, indicating decreased passivation property and higher corrosion sensitivity.

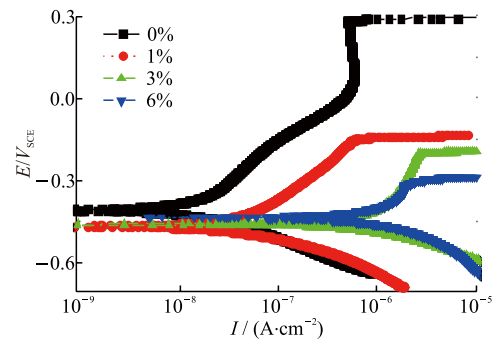


Fig.2 Polarization curves of the steel specimens in the pore solutions (pH 12.5) before and after different amounts of C-S-H treating

Fig.3(a) shows the Nyquist plots of the steel specimens in SPSs without or with 1%, 3%, and 6% C-S-H treating, respectively. It is seen that with the increase in C-S-H amount, the diameter of the semicircle reduces obviously, indicating the decrease of the steel impedance. The Randles circuit was used to model the EIS data, in which R_s represents the solution resistance, R_p is the polarization resistance of the corrosion process in micro-pores in the passive film and C_{CPE} is the double layer capacitance. R_p is in parallel with C_{CPE} and then in series with R_s . Fig.3(b) presents the effects of C-S-H amount on R_p of the steel in the SPSs. It can be seen that R_p decreases with the increase in the amount of C-S-H, especially in the solution with 3% or 6% C-S-H the decrease in R_p is obvious. So, by adding more C-S-H to pH 12.5 SPS the corrosion resistance of the steel can be reduced.

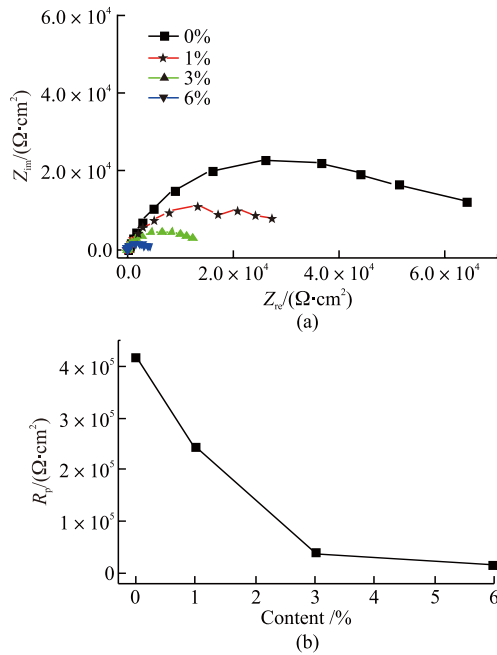


Fig.3 (a) Nyquist plot of the steel in the pore solutions (pH 12.5) before and after treating with different amounts of C-S-H. (b) Effects of C-S-H amount on R_p of the steel in solutions

Weight loss experiments were carried out in the

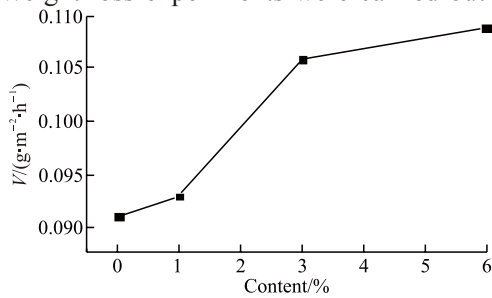


Fig.4 Variation of the corrosion rate of the steel specimens in the pore solutions (pH 12.5) before and after different amounts of C-S-H treating

SPSs. After immersion for 168 hours, the steel surface was cleaned with a 20% HCl plus 5% methenamine solution to remove the corrosion products. It was observed that in the solution without treating, corrosion occurred on some areas of the steel surface. After treating with 1%, 3%, and 6% C-S-H, the steel was corroded obviously. With more C-S-H added, the corroded areas extended more with some deep pits observed. Fig.4 shows the calculated corrosion rate of the steel. It is seen that with increasing C-S-H amount, the corrosion rate increases. At 1% addition, the variation in the corrosion rate is moderate. At 3% or 6% addition, the increase amplitude is obvious. This is consistent with the results from electrochemical tests.

The steel specimens were immersed in the SPSs without and with 3% C-S-H treating for 4 h, then cleaned with alcohol and analyzed by XPS method. The results are shown in Fig.5. According

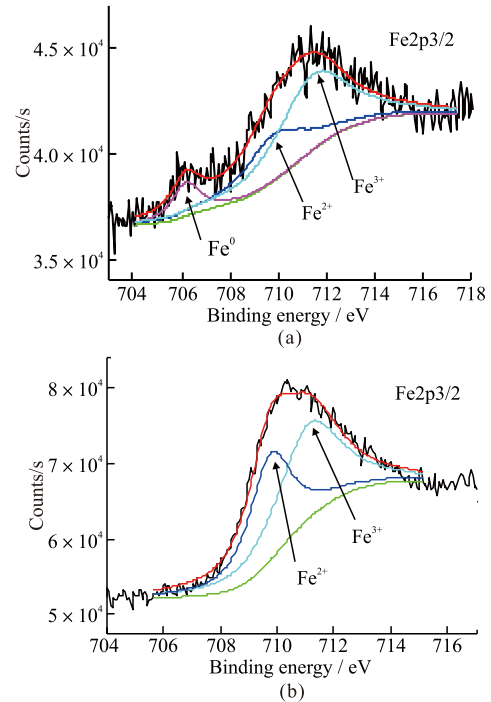


Fig.5 XPS analysis of the steel specimens in the pore solution (pH 12.5) before (a) and after (b) C-S-H treating (3wt%)

to literatures^[14-16], the passive film formed on carbon steel in pH 12.5 SPS may contain FeOOH, Fe₂O₃, FeO, and Fe₃O₄. In Fig.5(a) the binding energies of chemical species are Fe⁰ 2p₃ 706.6 ± 0.3 eV, Fe³⁺ 2p₃ 711 ± 0.3 eV, and Fe²⁺ 2p₃ 709.6 ± 0.3 eV. By fitting calculation, before treating the contents of Fe³⁺ and Fe²⁺ are 62.7% and 28.2%, respectively, and after treating the corresponding contents of Fe³⁺ and Fe²⁺ are 56.6% and 43.4%, respectively. The ratio between the concentration of Fe³⁺ and Fe²⁺ can be used to evaluate the protective property of the passive film^[14,15]. The higher the ratio of Fe³⁺/Fe²⁺, the higher content of FeOOH and Fe₂O₃ in the film, meaning better stability and protective performance. Conversely, the lower Fe³⁺/Fe²⁺ ratio, the higher content of FeO and Fe₃O₄, indicating worse stability and poorer protective performance of the film. It can be seen that after S-C-H treatment the Fe³⁺/Fe²⁺ ratio decreases apparently, meaning the drop in the stability of the film. This can explain the results of electrochemical tests and weight loss tests. Huet *et al*^[17] studied the influence of SPS pH on the film of mild steel and pointed out that in the SPS with pH values ranging from 13 to 10, a Fe³⁺ oxide film is formed on the steel surface which has good protective property. In SPS with pH value below 10, the film mainly consist of FeOOH and Fe₃O₄, in which Fe₃O₄ is poorly adhesive to the substrate.

3.3 Influences of C-S-H amount on pH value and chloride content of pH 9.7 SPS

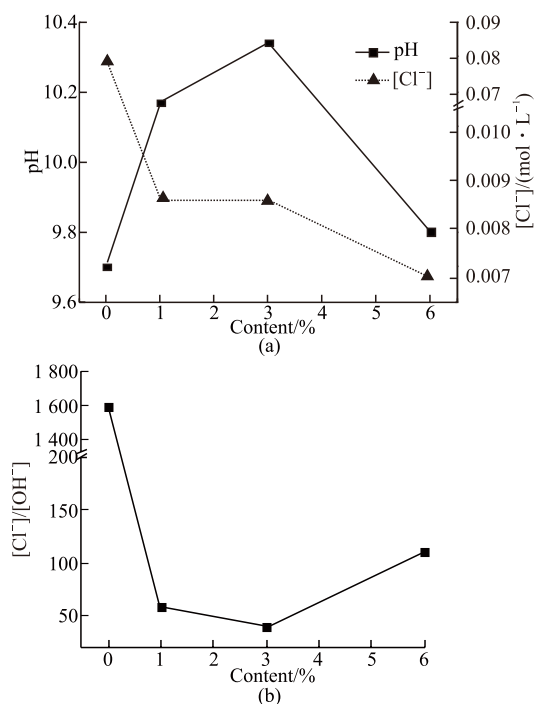
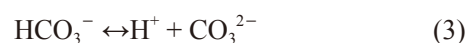
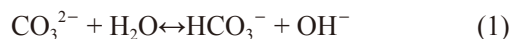


Fig.6 Influences of C-S-H amount (1%, 3% and 6%) on pH 9.7 pore solution: (a) pH and $[Cl^-]$, (b) $[Cl^-]/[OH^-]$

Fig.6 shows the variations of pH values and chloride contents in the SPSs before and after 1%, 3%, and 6% C-S-H treating, respectively. Before treating, the pH value was 9.7. It is seen in Fig.6(a) with increasing C-S-H amount, the pH value increases first and then decreases. From 1% to 3% addition, the pH value rises from 9.7 to 10.17 and 10.34, while at 6% addition, the value drops to 9.8. This is different from the result in the pH 12.5 SPS. The chloride contents in the SPSs all decrease remarkably after treating with different C-S-H amounts, which is about one tenth of the original content, showing no big difference from the result in pH 12.5 SPS. Fig.6(b) shows the variation of $[Cl^-]/[OH^-]$ ratio. It can be seen that before C-S-H treating, the ratio is very high (1596), which is far above the threshold $[Cl^-]/[OH^-]$ ratio for the onset of corrosion (0.66-1.40)^[13]. After C-S-H treating, the ratio decreases remarkably, which is 58.14, 39.31, and 110.94, respectively. The drop amplitude firstly decreases and then increases with the increase in the C-S-H addition, with the minimum value at the addition of 3%. So, 3% C-S-H treating has the biggest inhibitive effect on the steel corrosion behavior in pH 9.7 SPS, while 6% C-S-H treating has less effect compared with 1% and 3% C-S-H treating. But all the $[Cl^-]/[OH^-]$ ratios are still above the threshold of corrosion.

For pH 9.7 SPS, by treating with C-S-H the chloride ions content is decreased significantly, thereby decreasing the disruption by chloride ions. But the

more important is that the treating increases the pH effectively, which will contribute to the more stable film formed on the steel surface. The main compositions in pH 9.7 SPS are Na_2CO_3 and $NaHCO_3$. After C-S-H is added, Na^+ ions in the solution can substitute part of H^+ on the C-S-H structure surface so as to cause the rise of the acid H^+ ions concentration in the solution^[7-9]. While CO_3^{2-} and HCO_3^- ions in the solution will undergo hydrolysis according to formulae (1) and (2), HCO_3^- will ionize to some degree according to formula (3):



It is reported that^[18] in the alkaline aqueous solution containing CO_3^{2-} and HCO_3^- ions, when the pH value is between 8 to 10, the HCO_3^- concentration is higher than the CO_3^{2-} concentration, *i e*, HCO_3^- is the main existing form, which is due to the bigger extent of hydrolysis of CO_3^{2-} and HCO_3^- than the extent of HCO_3^- ionization. When C-S-H is added into the SPS, the substitution of Na^+ ions for H^+ on the C-S-H structure surface will result in the rise of H^+ ions concentration in the solution, thus reaction (3) will take place mainly from right to left, promoting the reaction (2) towards the right direction and causing the OH^- concentration rising and pH increasing. While with C-S-H increasing addition, when the pH is above 10 (pH 10.17 and 10.34 corresponding to 1% and 3% C-S-H, respectively), the CO_3^{2-} concentration is higher than the HCO_3^- concentration, *i e*, CO_3^{2-} is the main existing form. Meanwhile reaction (1) takes place mainly to the left and reaction (3) mainly to the right. So, the addition of 6% C-S-H causes the decrease in OH^- concentration thereby pH value decrease.

Because for pH 9.7 SPS, after C-S-H treating, with the increase in C-S-H amount (1%, 3%, and 6%), the amplitude of pH rising firstly increases and then decreases (the maximum value is at 3% addition), the drop amplitude of $[Cl^-]/[OH^-]$ rate first decreases and then increases, with the minimum value at the addition of 3% (Fig.6(b)). Above 3%, the corrosion risk of the steel in the solution will increase, instead.

3.4 Influence of C-S-H amount on the corrosion behavior of the steel in pH 9.7 SPS

Fig.7 shows the polarization curves of the steel specimens in the SPSs containing 0.08 mol/L Cl^-

before and after treating with 1%, 3%, and 6% C-S-H, respectively. The original pH of the solution was 9.7. It is shown that after C-S-H treating, the corrosion potential of the steel shifts to negative direction obviously, which indicates that the thermodynamic instability is improved. The corrosion current densities fitted by the polarization curves decrease. At 3% C-S-H addition, the current density is the smallest and the apparent passive region on the polarization curve is observed, indicating that under this condition, the steel has good passivation property and higher corrosion resistance.

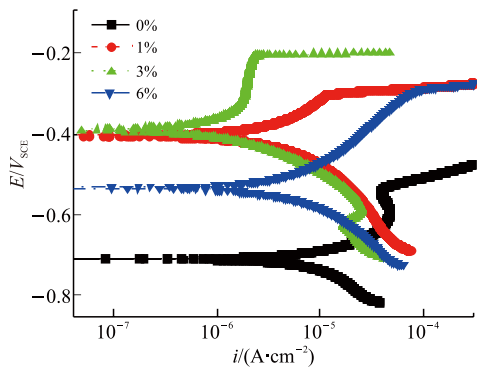


Fig.7 Polarization curves of the steel specimens in the pore solutions (pH 9.7) before and after different amounts of C-S-H treating

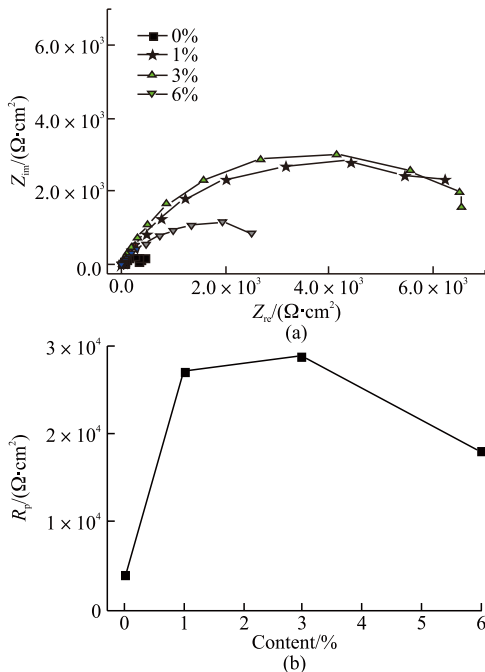


Fig.8 (a) Nyquist plot of the steel in the pore solutions (pH 9.7) before and after treating with different amounts of C-S-H. (b) Influences of C-S-H amount on R_p of the steel

Fig.8 shows the EIS plots of the steel in the SPSs before and after treating with 1%, 3%, and 6% C-S-H, respectively. It can be seen that after C-S-H

treating, the diameter of the semicircle increases, and the maximum is observed at 3% addition indicating the biggest impedance of the steel. Fig.3(b) presents the effects of C-S-H amount on R_p of the steel in the SPSs. It can be seen that R_p increases after C-S-H treating. This indicates that the film formed on the steel surface might become thicker or more compact and have better passivation property. With the increase in C-S-H addition, the rising amplitude of R_p increases at first and then decreases, with the turning point at 3% C-S-H. So, the C-S-H treating can improve the film stabilization on the steel surface in pH 9.7 SPS. The 1% addition has a good effect, 3% addition shows a better effect while at 6% addition the inhibition effect decreases. This is consistent with the polarization result.

Weight loss experiments were carried out for steel specimens in pH 9.7 SPSs before and after treating

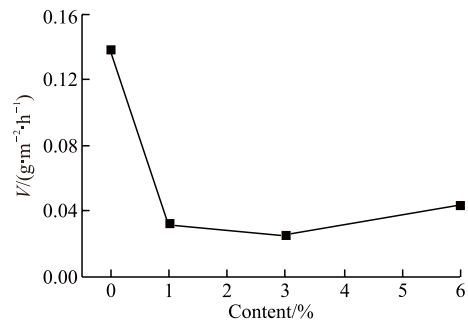


Fig.9 Variation of corrosion rate of the steel specimens in the pore solutions (pH 9.7) before and after treating with different amounts of C-S-H

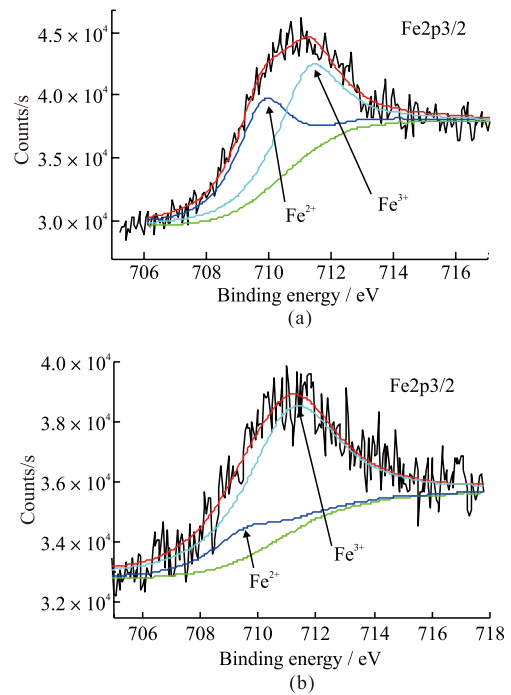


Fig.10 XPS analysis of the steel specimens in the pore solution (pH 9.7) before (a) and after (b) C-S-H treating (3wt%)

with 1%, 3%, and 6% C-S-H. It was found that the steel immersed in solution without treating suffered serious corrosion. After treating, the corrosion status was inhibited to different degrees. Among them, at 3% S-C-H addition, the steel suffered the slightest corrosion. Fig.9 shows the variation of the steel corrosion rate in the SPSs with C-S-H addition. After C-S-H treating, the corrosion rate decreases to one third of that before treating. The smallest corrosion rate occurs at 3% C-S-H addition, and then as the addition rises to 6%, the corrosion rate increases slightly. This is in accordance with the result of the electrochemical tests.

Fig.10 shows the XPS results of the steel specimens in the SPSs of pH 9.7. It is seen that before treating, Fe 2p spectrum is composed of two peaks corresponding to Fe^{2+} and Fe^{3+} . The contents of Fe^{3+} and Fe^{2+} by fitting calculation are 49.3% and 50.7%, respectively. After treating, the contents of Fe^{3+} and Fe^{2+} by fitting calculation are 84.3% and 15.7%, respectively, meaning that the main existing form of iron is Fe^{3+} , and the Fe^{3+}/Fe^{2+} ratio increases after S-C-H treatment. So, the S-C-H treating of the SPS (pH 9.7) could cause the film passivity on the steel enhanced. This can explain the results of the electrochemical and weight loss tests.

4 Conclusions

a) After treating with different amounts (1%, 3%, and 6%) of C-S-H, the $[Cl^-]/[OH^-]$ ratio in pH 12.5 SPS increases and the corrosion susceptibility of the steel increases with increasing amount of C-S-H. XPS result demonstrates that the Fe^{3+}/Fe^{2+} ratio in the film on steel surface decreases, leading to the drop of the passivity.

b) For pH 9.7 SPS, as the C-S-H amount increases, the $[Cl^-]/[OH^-]$ ratio decreases, with the lowest value at 3% C-S-H addition, which means that 3% C-S-H treating has the biggest inhibitive effect on the corrosion of steel.

c) The different effects are due to the influences of C-S-H on the pH values of solutions with different compositions. For pH 12.5 SPS, the strong alkaline binding property of C-S-H results in a decrease in pH value. For pH 9.7 SPS, the different increase degree in pH value might be closely related to the hydrolysis of CO_3^{2-} and HCO_3^- and the ionization of HCO_3^- , except for alkaline binding effect.

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