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Adsorption and Inhibition Behavior of Calcium Lignosulfonate on Steel in NaCl + Ca(OH)₂ Solutions with Different pH Values

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Potentiodynamic polarization measurements, microscopy infrared imaging (M-IR) and X-ray photoelectron spectroscopy (XPS) were used to study the adsorption and inhibition behavior of calcium lignosulfonate (CLS) on Q235 steel in 0.1 mol/L NaCl + Ca(OH)₂ solution (pH 7 ~ 12.5). In the solution of pH between 7 and 9.5, carbon steel was in active state. 0.001 mol/L CLS in the solution effectively inhibited both the cathodic and the anodic reactions. When the solution pH value increased to 9.5~10.5, passivation occurred and the main compositions of the passive film include Fe₂O₃, FeOOH, FeO and CaO/Ca(OH)₂. CLS promoted the passive state and raised the pitting corrosion potential E_b. In the solution of pH 7~9.5, an inhibition film formed by adsorption of the sulfonic acid group and benzene ring in CLS molecular on the surface. When the pH value increased to 10.5, a Ca-O-S co-adsorption structure could form between $-SO_3$ group in CLS and the outer side layer of the passive film which is composed of CaO/Ca(OH)₂. The strong adsorption characteristic between $-SO_3$ group in the adsorbed CLS on the surface and Ca²⁺ ions in solution may further improve the compactness of the adsorption film.

Keywords: Carbon steel; Corrosion; Inhibitor; CLS; Microscopy infrared imaging; XPS

1. INTRODUCTION

The reinforcement concrete is one of the most-widely used construction structural materials in modern industry. However, the degradation of reinforcement concrete structure has limited its applications and caused high repair costs [1]. It is well accepted that the most important causes for the reinforcement concrete degradation include the unreasonable design of the structure, carbonation of the concrete and corrosion of the reinforcing steel. The corrosion damage of the reinforcing steel is one of the main reason lead to the failure of the reinforcement concrete structure [2]. Generally, a thin passive film (< 10 nm) can form on the surface of rebar due to the high pH value in concrete [3]. Sometimes

the pH value of the concrete pore solution may decrease considerably when the concrete is used in some aggressive environments. The composition and state of the passive film could be influenced by the pH value, which would result in corrosion damage of the rebar [4-6]. Researchers has studied the passive behavior of rebar and the composition of passive film in simulated concrete pore solution of different pH values. Moreno et al. [7] studied the influences of chloride ions and carbonation on reinforcing steel in eight kinds of simulated concrete pore (SCP) solutions with different pH values. The results showed that the high pH value could prevent pitting corrosion. The steel could not get passivated when the concrete became carbonated and combined with chloride ions at the same time. The transition pH for passivation was between $9.4 \sim 10$. Freire et al. [8] studied the influence of pH value on the electrochemical behavior of reinforcing steel in alkaline solutions with chlorides. The results showed that the pH value of the solution had a significant influence on the film resistance (R₁) and charge transfer resistance (R₂). The resistance R₁ decreased whereas the resistance R₂ increased as the pH changed from 13 to 9. The ferrite compounds dissolved more readily at a lower pH value.

The application of inhibitors is a useful protection method to prevent the rebar from corrosion. The inorganic inhibitors based on nitrites have shown good inhibition performance for reinforcing steel since 1960s. Many researchers studied the inhibition mechanism of nitrites. Garces et al. [9] invested the inhibition properties of the nitrites compounds on carbon steel in SCP solutions with different pH values. Nitrites showed good inhibition efficiency for carbon steel in SCP solution with low concentration of chloride. But the inhibition efficiency of nitrites decreased with the decreasing of pH value. The results suggested that the pH value of simulated concrete pore solution may influence not only the composition and property of passive film, but also the inhibition efficiency of the inhibitor, showed good inhibition performance on Q235 carbon steel in simulated concrete pore solution of pH 12.6. CLS was good for both general corrosion and pitting corrosion on carbon steel and the inhibition efficiency of CLS was higher than 98%. However, in practical use the acidification of concrete may become an important factor affecting the adsorption and inhibition behavior of CLS on carbon steel.

The purpose of this work is to understand the influence of pH value on the adsorption and inhibition behavior of CLS on carbon steel in simulated concrete pore solution. The passivation behavior of carbon steel and the inhibition efficiency of CLS are investegated with potentiodynamic polarization measurement, microscopy infrared imaging (M-IR) and X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL METHODS

The studied materials was Q235 carbon steel with following chemical composition (w%): C 0.11%; Si 0.13%; Mn 0.74%; S 0.0028%; P 0.012%; O 0.010%; N 0.0040% and Fe bal. The working electrode for electrochemical measurement was cut into 8 mm \times 8 mm \times 10 mm coupons, polished with abrasive papers up to 1000 grits, rinsed with distilled water, degreased in acetone and dried. The test solution was 0.1 mol/L NaCl solution, and the pH value of the solution was adjusted to 7, 8.5, 9.5, 10.5, 11.5 and 12.5 respectively by adding Ca(OH)₂. Distilled water and analytical grade chemicals

were used for this study. The purity of calcium lignosulfonate (CLS) used in this test was 96% and the adding amount was 0.001 mol/L, which hardly changed the pH value of the test solution.

The electrochemical measurements were carried out with a CS350 electrochemical workstation. A three-electrode system was used in this study. The working electrode was the carbon steel sample with the exposure area of 0.04 cm². The auxiliary electrode was a platinum electrode and the reference electrode was a silver/silver chloride electrode (SSC). Before the polarization test, the open circuit potential was measured for 1h. The potential scanning range was from -300 mV to +1000 mV versus OCP. The scan rate was $0.3 \text{ mV} \cdot \text{s}^{-1}$. Five polarization curves were measured at each test condition to estimate the reproducibility.

The microscopy infrared imaging (M-IR) system used in this study was a Spotlight 400 Microscopy & Imaging Systems (Perkin-Elmer, USA). Before the M-IR test, samples were immersed into the Ca(OH)₂ + 0.1 mol/L NaCl solution of different pH values with or without inhibitors for 10 h. After 10 h immersion, the samples were carefully removed and dried. The spatial resolution was 6.25 μ m and the spectroscopy resolution was 16 cm⁻¹. The scan number was 30 and the test area was 50×50 μ m.

The X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250 spectrometer (Thermo Fisher Scientific, USA). Before the XPS measurement, the samples were immersed in the test solution for 10 h. The preparation of samples was the same with the samples used in M-IR test. Three parallel samples were prepared for each test condition. The binding energy values were calibrated by the C1s peak at 285 eV. The data processing was done with a XPS-Peaks 4.1 program.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurement

Fig. 1 shows the polarization curves of carbon steel in the $Ca(OH)_2 + 0.1$ mol/L NaCl solution of different pH values with and without inhibitors. The fitting data of the polarization curves were calculated by C-view software [10] and illustrated respectively in Table 1 and Table 2.

As shown in Fig. 1, when the pH value was 7~8.5, carbon steel was in active state without adding inhibitor. The corrosion rates were relatively fast. When the pH value increased to 9.5, the polarization behavior changed from active corrosion to passivation with a passive region about 100 mV in width. With the pH value increased, the passive region extended, which is due to improved passivation by the increased OH content in the test solution [7]. When the pH value increased over 11.5, the pitting potential (E_b) increased significantly and the passivation region were wider than 400 mV. At the pH value of 12.5, the E_b value was -38 mV, the E_{corr} value was -395 mV and the width of the passive region was about 360 mV. The anodic slopes (β_a) of the polarization curves increased as the pH value increased, indicating that the anodic dissolution of metal was hindered at higher pH value. The results are similar to previous report [10].

After adding CLS, the polarization behavior of steel in the test solution was almost the same with those without adding inhibitor. However, at pH 7 and 8.5, the corrosion current densities decreased obviously after addition of CLS (Figs. 1a and 1b) and both the cathodic and the anodic processes were inhibited.



Figure 1. Polarization curves of Q235 steel in $Ca(OH)_2$ +NaCl solutions of different pH values with and without 0.001 mol/L CLS: (a) pH = 7; (b) pH = 8.5; (c) pH = 9.5; (d) pH = 10.5; (e) pH = 11.5; (f) pH = 12.5.

At pH values higher than 9.5, both the corrosion current densities decreased and the passive regions extended significantly (Figs. 1c through 1f). With the pH value of the solution increased from 9.5 to 12.5, the E_b value increased from -48 mV to 568 mV, indicating that CLS could effectively prevent pitting corrosion of steel in the tested system. After adding CLS in the solution, both the

cathodic (β_c) and the anodic (β_a) slopes of the polarization curves increased compared with the values without inhibitor (Table 1), which indicates that both the anodic and cathodic reactions were inhibited by CLS [11-13]. The polarization results show that CLS was a mix-type inhibitor [13] and mainly inhibit the anodic process [10]. The inhibition effect of CLS may be attributed to the adsorption film formed on the steel surface which would hinder the adsorption of chloride ions onto the surface [14].

pH value	$-\beta_c (mV \cdot dec^{-1})$		$\beta_a(mV \cdot dec^{-1})$		$i_{corr}(mA/cm^2)$	
	without CLS	with CLS	without CLS	with CLS	without CLS	with CLS
7	81	96	33	41	1.49×10 ⁻⁵	5.73×10 ⁻⁶
8.5	82	101	43	65	8.16×10 ⁻⁶	3.11×10 ⁻⁶
9.5	85	99	109	115	2.95×10 ⁻⁶	1.03×10 ⁻⁶
10.5	91	104	112	124	5.32×10 ⁻⁶	7.91×10 ⁻⁷
11.5	105	109	117	134	3.19×10 ⁻⁶	4.52×10 ⁻⁷
12.5	109	112	131	139	1.24×10 ⁻⁶	1.63×10 ⁻⁷

Table 1. Parameters obtained via Tafel extrapolation of the polarization curves.

 $IE\% = (i_{corr without CLS} \cdot i_{corr with CLS}) / i_{corr without CLS}; \Delta E_b = E_b with CLS - E_b without CLS.$

pH value	$E_{corr}(mV)$		$E_b(mV)$		IE (%)	$\Delta E_b (mV)$
	without CLS	with CLS	without CLS	with CLS	with CLS	with CLS
7	-297.81	-	-	5.73×10 ⁻⁶	61.54	-
8.5	-305.74	-	-	3.11×10 ⁻⁶	61.88	-
9.5	-333.87	-207.65	-207.65	1.03×10 ⁻⁶	65.08	272.73
10.5	-292.35	-178.01	-178.01	7.91×10 ⁻⁷	85.13	396.04
11.5	-310.08	-95.03	-95.03	4.52×10 ⁻⁷	85.79	492.84
12.5	-395.15	-48.71	-48.71	1.63×10 ⁻⁷	86.85	616.74

Table 2. Parameters obtained from the polarization curves.

3.2. Microscopic infrared imaging method (M-IR)

In order to further examine the adsorption and inhibition behavior of CLS on carbon steel in the test solutions, M-IR analysis was carried out for the samples which were immersed in $Ca(OH)_2 + 0.1$ mol/L NaCl solutions of different pH values with or without addition of CLS. The adding amount of CLS was 0.001 mol/L. The test area on the samples was 50×50 µm. To ensure the accuracy of the test, on each sample three different areas have been observed. The M-IR spectra are composed of the visual

image, the IR image and the FT-IR spectra. The visual image shows the appearance of samples, and the IR image which corresponded to the visual image illustrates the distributions of the adsorbed species. Different colors in IR images present different absorbance of species adsorbed on the surface (lighter color presented stronger absorbance). The FT-IR spectra corresponded to the selected spots on the IR images, which show the type and structure of the adsorbed species or groups at the spots.

The M-IR spectra of carbon steel without immersion are shown in Fig. 2 as comparison. On the original steel surface the grinding marks can be observed on the visual image of Fig. 2a. Fig. 2b shows the corresponding IR image. The FT-IR spectra for marked spots (No. 1 and No. 2 in Fig. 2b) are illustrated as Fig. 2c. It can be seen that for the sample without immersion there are no discernible adsorbed species on the surface.



Figure 2. M-IR images of Q235 steel samples before immersion: a: Visible images; a': Corresponding IR image; a": FT-IR spectra of the marked areas in IR image

Fig. 3 shows the M-IR images for samples immersed in $Ca(OH)_2 + 0.1 \text{ mol/L NaCl}$ solutions of different pH values with or without CLS. Figs. 3a through 3f and Figs. 3a' through 3f' are the visual images of samples immersed in solutions with and without inhibitors respectively. Figs. 3a'' through 3f'' and Figs. 3a''' through 3f''' are the IR images corresponding to the visual images. The IR spectra for the selected spots on the IR images (No.1~No.24 in Fig. 3) are illustrated in Fig. 4.



Figure 3. M-IR images of samples immersed in Ca(OH)₂+NaCl solutions of different pH values without (a-f, a'-f') and with CLS (a"-f", a"'-f"'): (a) pH = 7; (b) pH = 8.5; (c) pH = 9.5; (d) pH = 10.5; (e) pH = 11.5; (f) pH = 12.5.

At the pH value of 7~8.5, shown in Fig. 3a and Fig. 3b, large corroded areas appeared on the sample immersed in solution without CLS. The surface appearance changed obviously by adding CLS,

as shown in Fig. 3a" and Fig. 3b". Many pits can be seen on the surface but the pits did not expand to large corroded areas, suggesting that the general corrosion was retarded to some extent by adding CLS. For the selected spots (No.1-No.8) in Figs. 3a', 3a", 3b' and 3b", the FT-IR spectra are shown in Fig. 4a and Fig. 4b. After adding CLS, a tri-peak around 1400~1600 cm⁻¹ can be distinguished in FT-IR spectra.



Figure 4. FT-IR spectra of the marked areas in Figure 4: (a) pH = 7; (b) pH = 8.5; (c) pH = 9.5; (d) pH = 10.5; (e) pH = 11.5; (f) pH = 12.5.

The peak is correspondent to the benzene ring of sinapyl alcohol monomer, which is a typical functional group of CLS molecular [15]. The peak intensities at the spots around pits or at the areas without obvious corrosion are similar, which suggests that the adsorption of CLS on the surface was uniform.

When the pH value was raised to $9\sim10.5$, as shown in Fig. 3c and Fig. 3d, for samples immersed in solution without CLS, large corroded areas disappeared with many small pits instead on the surface. With CLS added, some corroded areas about $5\sim10 \ \mu\text{m}$ in diameter can be seen but the number of the corroded spots were mach smaller (Fig. 3c" and Fig. 3d"). The FT-IR spectra (Fig. 4c and Fig. 4d) for the selected spots (No.9-No.16) indicate that the adsorption of CLS on the surface was stronger. In addition, the result in Fig. 4c^m suggests that the adsorption of CLS around the corroded spots was stronger than on other areas.

When the pH value of solution was further increased to $11.5 \sim 12.5$, the number and size of pits on samples immersed in solutions without CLS were significantly reduced (Fig. 3e and Fig. 3f), leaving a few locally corroded areas. After adding CLS, corrosion was effectively prevented. Also the preferential adsorption of CLS around pits can be seen, which confirms our previous observation in a saturated Ca(OH)₂ + 0.1 mol/L NaCl solution with pH 12.6 [15].

At the pH value of 7~8.5, general corrosion happened on the steel surface and Fe^{2+} ions were produced [16]. According to HASB theory [17], the matrix Fe is a kind of soft acid, Fe^{2+} ion is a borderline acid while benzene ring in CLS molecular is a kind of soft base [18]. The soft base could react with the soft acid and the borderline acid, leading to the adsorption of CLS both on the matrix and on the corroded areas. The adsorption of CLS would form an adsorption film to protected the matrix from corrosion and prevented the adsorption of chloride ions onto the surface [19].

Huet et al. [3] found that the transition pH of mild steel in concrete pore solution was between 9.4~10. When the pH value was higher than 9.5, a thin iron III oxide layer generally formed on the steel surface [20-22]. The Fe^{3+} is a hard acid while the matrix Fe is a soft acid [17]. The benzene ring of sinapyl alcohol monomer in CLS could preferentially adsorb on the matrix Fe rather than on Fe^{3+} and effectively protect the matrix which is not covered by the passive film.

At the pH value between 10~13, passive film forms on the surface [3]. When the pH value is higher than 10.5, the passive film protects the steel effectively, resulting in extended passivation region on the polarization curves [23]. When CLS is added, the sinapyl alcohol monomer would preferentially adsorb on Fe and Fe²⁺ ions. As the results the locally corroded areas would be the preferentially adsorbed areas for CLS [18]. According to Macdonald et al's point defect model [24-28], the transport and local accumulation of point defects in passive films such as the cation vacancies and the oxide vacancies would cause the breakdown of the passive film. The adsorption of inhibitors could fill up the defects on passive film and reduce the concentration of point defects [29, 30], increasing the protective properties of passive film [31]. At the same time, the adsorption of inhibitors on the passive film may form an "adsorption-passive" double film structure which could have a better inhibition efficiency due to the barrier effect to chloride ion and water molecule [32]. Therefore, CLS could improve the passive ability and have a positive shift on the pitting potential.

3.3. X-ray photoelectron spectroscopy analysis (XPS)

3.3.1. Wide-scan XPS spectra

XPS analysis was carried out to study the inhibition mechanism of CLS in the studied system. The binding energy peaks were calibrated by the value of C1s peak at 285 eV. Fig.5 shows the widescan XPS spectra of the samples immersed in $Ca(OH)_2 + 0.1$ mol/L NaCl solutions with different pH values for 10 h. As shown in Fig. 5a, without adding CLS, only C, O, Fe and Cl could be detected on the surface at the pH value of 7~9.5. With the pH value increased to 10.5~12.5, the peaks of Fe obviously changed and Ca could be detected on the sample surface.



Figure 5. Wide-scan XPS spectra of samples after immersion for 10 h in Ca(OH)₂+NaCl solutions of different pH values: (a) without inhibitor; (b) with 0.001 mol/L CLS.

After adding inhibitors, peaks of C, O, Fe, Ca, S and Cl are observed in Fig. 6b. The addition of CLS increased the contents of Ca and S on the surface. The presence of S could confirm the adsorption of CLS because CLS was the only source in this study containing S. The intensity of Ca peak in Fig. 6b is higher than that in Fig. 6a, which may be due to the adsorption of CLS.

3.3.2. The passive film formed in solution of different pH value without CLS

Fig. 6 and Fig. 7 show Fe $2p_{3/2}$ and O 1s spectra of the samples immersed in Ca(OH)₂ + 0.1 mol/L NaCl solutions of different pH values for 10 h. As shown in Fig. 6a, at the pH value of 9.5, ferrite was present on the surface as Fe₂O₃ (710.6 ± 0.3 eV [33]) and FeOOH (711.2 ± 0.3 eV [33]). The broad peak at 712.7 eV is the satellite peak of Fe₂O₃, as illustrated in other studies [34]. The peak of O 1s at 530.0 ± 0.2 eV in Fig. 7a, which is related to O²⁻, confirms the presence of Fe₂O₃ [34, 35]. The peaks at 530.5 ± 0.2 eV and 531.4 ± 0.3 eV are attributed to O²⁻ [33] and OH⁻ [34, 36] in FeOOH. The results of polarization test and M-IR test showed that general corrosion happened on the surface when pH value was 7~9.5. According to the XPS results, the main corrosion products should be Fe₂O₃ and FeOOH.

The Fe $2p_{3/2}$ spectra of samples immersed in test solution of pH 10.5 are shown in Fig. 6b. Besides the peaks of Fe₂O₃ (710.6 ± 0.3 eV [33]) and FeOOH (711.2 ± 0.3 eV [33]), small peaks at 706.6 eV and 708.4 eV are observed which should be attributed to Fe⁰ (706.6 ± 0.2 eV [37]) and FeO (708.4 \pm 0.3 eV [38]), respectively. The Fe⁰ should be attributed to the matrix. O 1s spectra are shown in Fig. 7b, and the presence of ferrite oxides and hydroxides are confirmed. The two peaks at 530.3 eV and 532.6 eV should be due to the presence of CaO [34] and Ca(OH)₂ [35]. Because the pH value of the test solution was adjusted by adding Ca(OH)₂, with increasing pH value, the content of Ca(OH)₂ in the solution increased at the same time. A layer of CaO/Ca(OH)₂ may present on the surface. Page et al. [39, 40] suggested that steel may be protected by a layer of Ca(OH)₂, which could effectively retard the catholic reaction and prevent corrosion. Page had put forward a hypothesis that "the passive film was composed of different structures", namely the outer layer of the passive layer was consisted of calcium oxide/hydroxide and the inner layer of the passive film was ferrite oxide/hydroxide [41]. Yonezawa et al. [42] reported that a discontinuous layer of Ca(OH)₂ formed on metal in saturated Ca(OH)₂ solution which provided a protection performance to the matrix. Frateur et al. [43] confirmed the enrichment of Ca on the passive film in alkaline solution containing calcium ions, mainly presenting as Ca(OH)₂. Fig. 8 shows the peaks of Ca. The peaks of Ca at 347.7 eV and 351.7 eV are respectively due to Ca $2p_{3/2}$ [44] and Ca $2p_{1/2}$ [45] of CaO/Ca(OH). When the solution pH value increased to 12.5, the peaks of Fe, O and Ca showed similar results.

In short, in the test solution at the pH value of $7 \sim 8.5$ without CLS, general corrosion happened on steel surface. The main composition of the corrosion products were Fe₂O₃ and FeOOH. When the pH value increased to 10.5~12.5, a passive film formed on the surface which mainly composed of Fe₂O₃, FeOOH, FeO and CaO/Ca(OH)₂.



Figure 6. Fe $2p_{3/2}$ XPS spectra of sample immersed in Ca(OH)₂+NaCl solutions of different pH values for 10 h. (a) pH = 7; (b) pH = 10.5.



Figure 7. O 1s XPS spectra of sample immersed in Ca(OH)₂+NaCl solutions of different pH values for 10 h. (a) pH = 7; (b) pH = 10.5.



Figure 8. Ca 2p XPS spectra of sample immersed in Ca(OH)₂+NaCl solution of pH 10.5 for 10 h.

3.3.3. Passive-adsorption film formed in solutions of different pH values with CLS



Figure 9. Fe $2p_{3/2}$ XPS spectra of sample immersed in Ca(OH)₂+NaCl + CLS solutions of different pH values for 10 h. (a) pH = 7; (b) pH = 10.5.



Figure 10. O 1s XPS spectra of sample immersed in Ca(OH)₂+NaCl+ CLS solutions with of different pH values for 10 h. (a) pH = 7; (b) pH = 10.5

Further, XPS spectra of samples after immersion for 10 h in $Ca(OH)_2 + 0.1 \text{ mol/L NaCl} + 0.001 \text{ mol/L CLS}$ solutions with different pH values were measured. Fig. 9 and Fig. 10 show the Fe $2p_{3/2}$ and O 1s spectra. It is seen in Fig. 9a and Fig. 10a that at the pH value of 7~9.5 Fe was present on sample surface as Fe₂O₃ and FeOOH. A broad peak at 533.4 eV appears in O 1s spectra, which is

attributed to the peak of organic compounds reported by other researchers [34] and may be due to the adsorption of CLS.

When the pH value increased to 10.5, Fe was present mainly as Fe_2O_3 , FeOOH and FeO (Fig. 9b). The peaks of CaO/Ca(OH)₂ also can be detected in the O 1s spectra. At the pH value of 7~8.5, the main composition of corrosion products formed on the surface were Fe_2O_3 and FeOOH. When the pH value was higher than 10.5, the surface was composed mainly of Fe_2O_3 , FeOOH, FeO and CaO/Ca(OH)₂. The addition of CLS in solution did not change the composition of the passive film.

The peaks of Ca and S were measured to understand the adsorption behavior of CLS. Because calcium may derive from both Ca(OH)₂ in solution and CLS molecular, the Ca and S spectra of CLS were firstly measured. As shown in Fig. 11, three peaks appear in the Ca 2p spectra which are at 347.9 eV, 351.6 eV and 344.7 eV respectively. The peaks at 347.9 eV and 351.6 eV are attributed to Ca $2p_{3/2}$ [44] and Ca $2p_{1/2}$ [45]. These two peaks are similar to those of CaO/Ca(OH)₂ and may be attributed to Ca-LS structure. While the peak at 344.7 eV is attributed to Ca²⁺ ions [46]. The Ca²⁺ ions may be due to the dissociation of CLS caused by moisture in the air. Fig. 11b is the S $2p_{3/2}$ spectra of CLS and two peaks are seen at 165 eV and 168.8 eV, respectively. The peak at 165.2 eV is S $2p_{1/2}$ [47] while that at 168.8 eV is S in –SO₃ group in CLS molecular [48].



Figure 11. XPS spectra of CLS powders: (a) Ca 2p; (b) S 2p_{3/2}.

Fig. 12 shows Ca 2p spectra of the sample immersed in Ca(OH)₂ + 0.1 mol/L NaCl + 0.001 mol/L CLS solution with different pH values for 10 h. Previous result in Fig. 5 has shown that without adding CLS, the peaks of Ca on the surface can be only detected when the solution pH increased to 10.5~12.5, hence the presence of Ca should be related to the formation of the passive film. However, with CLS added, in the test solution of pH 7~9.5 Ca was also detected and the binding energy values of the double peaks of Ca 2p are respectively 347.4 eV and 351.3 eV (Fig. 12a) which are slightly lower than the values of CLS powders (347.9 eV and 351.6 eV in Fig. 11a). Hence it may be assumed that the analyzed Ca was present not in CLS molecular, but more probably in the Ca-LS adsorption structure. This result suggests that CLS was not directly adsorbed on the surface in molecular state but might be firstly dissociated into Ca²⁺ and LS⁻ ions in solution, then the LS⁻ and Ca²⁺ ions adsorb on the surface and form Ca-LS structure. Ouyang et al. [49] studied the adsorption between sodium ligninsulfonate molecular and CaCO₃. The sulfonic acid group showed a strong adsorption to Ca.

Cizaire et al. [50] also reported the strong adsorption characteristic of $-SO_3$ group to Ca^{2+} ions in solution. Therefore the $-SO_3$ group in LS^- ions adsorbed on the steel surface would have a strong adsorption to Ca^{2+} ions in the solution.



Figure 12. Ca 2p XPS spectra of sample immersed in Ca(OH)₂+NaCl+ CLS solutions of different pH values for 10 h. (a) pH = 7; (d) pH = 10.5.

When the pH value increased to 10.5, a peak at 347.5 eV appeared in Ca 2p spectra. This peak should be attributed to the Ca-O-S "co-adsorption" structure formed between $-SO_3$ group in CLS molecular and Ca enriched on the passive film [15]. As mentioned in the earlier discussion of Figs. 6 through 8, a CaO/Ca(OH)₂ layer may be formed on the surface at the pH values of 10.5~12.5. When the pH value increased to 12.5, the Ca 2p spectra showed similar result.

The co-adsorption structure can be confirmed by the S $2p_{3/2}$ spectra. It is seen in Fig. 13a that at the pH value of 7~9.5 the peak of S is at 168.7 eV, close to the binding energy of S in $-SO_3$ group (168.8 eV [48]). The peak should be attributed to LS⁻ ions adsorbed on the surface. At the pH values of 10.5~12.5, the peak of S shifted to 168.1 eV, which is the same to the binding energy of S $2p_{3/2}$ in Ca-O-S structure (168.1 eV [15]). The inhibition efficiency of CLS in solutions with pH values of 10.5~12.5 is higher than in solutions of pH 7~8.5, which may be due to the Ca-O-S co-adsorption structure.



Figure 13. S 2p_{3/2} XPS spectra of sample immersed in Ca(OH)₂+NaCl+CLS solutions of different pH values for 10 h. (a) pH = 7; (d) pH = 10.5.

3.3.4. Mechanism of the adsorption of CLS in solution of different pH value

The above results confirm that in the test solution with pH values of 7~9.5, carbon steel was in active state and CLS could effectively inhibit both the cathodic and the anodic reactions. The polar groups in CLS molecular include sinapyl alcohol monomer (containing benzene ring and methoxy group) and sulfonic acid group. The sulfonic acid groups or phosphate groups in organic molecular could form a coordinate bond through sharing the lone pair of electrons with the d-orital of Fe or the oxygen vacancies in the passive film [51, 52], while the benzene ring in sinapyl alcohol monomer could also form a coordinate bond with Fe [53] and adsorb on steel surface. The adsorption of CLS forms an adsorption film which would barrier the adsorption of chloride ions on the surface [10], preventing the steel from corrosion.

When the pH value of the solution reached 10.5, the steel was passivated and a passive film formed on the surface [3]. The main compositions of the passive film include Fe₂O₃, FeOOH, FeO and CaO/Ca(OH)₂. The sulfonic acid group of CLS has a strong adsorption characteristic with Ca [49, 50]. CLS could form a Ca-O-S co-adsorption [15] structure with the outer side layer of the passive film which is composed of the oxides/hydroxides of calcium. The strong adsorption characteristic between $-SO_3$ group in the adsorbed CLS on the surface and Ca²⁺ ions in solution may improve the compactness of the adsorption film on the surface, as shown in Fig. 14. As the result, under the condition of higher pH, both the passive film and the compact CLS inhibition film effectively retard the corrosion process of the steel.



Figure 14. Schematic illustration of the adsorption between LS^{-} molecular and Ca^{2+} .

4. CONCLUSIONS

(1) In Ca(OH)₂ + 0.1 mol/L NaCl solution with pH value between 7 and 9.5, carbon steel was in active state. 0.001 mol/L CLS in the solution effectively inhibited both the cathodic and the anodic reactions. When the solution pH value increased to $9.5 \sim 10.5$, passivation occurred and the main compositions of the passive film include Fe₂O₃, FeOOH, FeO and CaO/Ca(OH)₂. CLS could promote

the passive state and raise the pitting corrosion potential E_b . With increased pH value, the E_b value was further increased by adding CLS.

(2) In the solution of pH 7~9.5, an inhibition film formed by adsorption of the sulfonic acid group and benzene ring in CLS molecular on the surface. When the pH value increased to 10.5, a Ca-O-S co-adsorption structure could form between $-SO_3$ group in CLS and the outer side layer of the passive film which is composed of CaO/Ca(OH)₂. The strong adsorption characteristic between $-SO_3$ group in the adsorbed CLS on the surface and Ca²⁺ ions in solution may further improve the compactness of the adsorption film.

(3) The M-IR results indicate that in the solution of pH 11.5~12.5 CLS showed preferential adsorption at the locally corroded spots on steel surface, which would be beneficial for the inhibition to localized corrosion.

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References

- 1. S. Ahmad. Cem. Concr. Compos., 25 (2003) 459-471.
- 2. M. Montemor, A. Simoes, M. Ferreira. Cem. Concr. Compos., 25 (2003) 491-502.
- 3. B. Huet, V. L'Hostis, F. Miserque, H. Idrissi. *Electrochimi. Acta*, 51 (2005) 172-180.
- 4. P.K. Mehta, R.W. Burrows. Concr. Int., 23 (2001) 57-63.
- 5. X. Feng, Y. Zuo, Y. Tang, X. Zhao, X. Lu. *Electrochim. Acta*, 58 (2011) 258-263.
- 6. S. Ramadan, L. Gaillet, C. Tessier, H. Idrissi. Appl. Surf. Sci., 254 (2008) 2255-2261.
- 7. M. Moreno, W. Morris, M. Alvarez, G. Duffo. Corros. Sci., 46 (2004) 2681-2699.
- 8. L. Freire, M. Carmezim, M. Ferreira, M. Montemor. *Electrochim. Acta*, 56 (2011) 5280-5289.
- 9. P. Garcés, P. Saura, E. Zornoza, C. Andrade. Corros. Sci., 53 (2011) 3991-4000.
- 10. X. Zhou, H. Yang, F. Wang. Corros. Sci., 54 (2012) 193-200.
- 11. L.C. Murulana, M.M. Kabanda, E.E. Ebenso. J. Mol. Liq., 215 (2016) 763-779.
- 12. I. Zaafarany, M. Abdallah. Int J Electrochem Sci, 5 (2010) 18-28.
- 13. M. Abdallah, E. Helal, A. Fouda. Corros. Sci., 48 (2006) 1639-1654.
- 14. M. Yamaguchi, H. Nishihara H, K. Aramaki K. Corros. Sci., 1994, 36(2): 241-258.
- 15. Y. Wang, Y. Zuo, X. Zhao, S. Zha. Appl. Surf. Sci., 379 (2016) 98–110.
- 16. W. Chen, R. Du, C. Ye, Y. Zhu, C. Lin. Electrochimi. Acta, 55 (2010) 5677-5682.
- 17. S. Martinez, L. Valek, I.S. Oslaković. J. Electrochem. Soc., 154 (2007) C671-C677.
- 18. Y. Wang, Y. Zuo. Corros. Sci., under review.
- 19. T. Szauer, A. Brandt. Electrochimi. Acta, 26 (1981) 1257-1260.
- 20. C.M. Hansson. Cambridge Univ Press, 1985, pp. 475.
- 21. M.i. Nagayama, M. Cohen. J. Electrochem. Soc., 109 (1962) 781-790.
- 22. J. Kruger. Corros. Sci., 29 (1989) 149-162.
- 23. J. Soltis. Corros. Sci., 90 (2015) 5-22.
- 24. C. Chao, L. Lin, D. Macdonald. J. Electrochem. Soc., 128 (1981) 1187-1194.
- 25. C. Chao, L. Lin, D. Macdonald. J. Electrochem. Soc., 129 (1982) 1874-1879.
- 26. M. Urquidi, D.D. Macdonald. J. Electrochem. Soc., 132 (1985) 555-558.
- 27. M. Urquidi Macdonald, D.D. Macdonald. J. Electrochem. Soc., 134 (1987) 41-46.
- 28. D. Macdonald, M. Urquidi-Macdonald. Corros. Sci., 31 (1990) 425-430.

- 29. K. Khaled, M.A. Amin. J. Appl. Electrochem., 38 (2008) 1609-1621.
- 30. A.Y. Musa, R.T. Jalgham, A.B. Mohamad. Corros. Sci., 56 (2012) 176-183.
- 31. Z.H. Dong, W. Shi, G.A. Zhang, X.P. Guo. *Electrochimi. Acta*, 56 (2011) 5890-5897.
- 32. G. Sahoo, R. Balasubramaniam. Corros. Sci., 50 (2008) 131-143.
- 33. F. Miserque, B. Huet, G. Azou, D. Bendjaballah, V. L'Hostis. J. Physi. IV, (2006), 89-97.
- 34. P. Ghods, O. Isgor, J. Brown, F. Bensebaa, D. Kingston. Appl. Surf. Sci., 257 (2011) 4669-4677.
- 35. N. Nakayama, A. Obuchi. Corros. Sci., 45 (2003) 2075-2092.
- 36. N. McIntyre, D. Zetaruk. Anal. Chemi., 49 (1977) 1521-1529.
- 37. X. Feng, Y. Tang, Y. Zuo. Corros. Sci., 53 (2011) 1304-1311.
- 38. A. Grosvenor, B. Kobe, M. Biesinger, N. McIntyre. Surf. Interface Anal., 36 (2004) 1564-1574..
- 39. C. Page, Nature, 258 (1975) 514-515.
- 40. C. Page. Nature, 297 (1982) 109-115.
- 41. D. Leek, AB Poole in: Page CL, Treadway KW, Bamforth PB. Appl. Sci, 1990
- 42. T. Yonezawa, V. Ashworth, R. Procter. Corrosion, 44 (1988) 489-499.
- 43. I. Frateur, A. Carnot, S. Zanna, P. Marcus. Appl. Surf. Sci., 252 (2006) 2757-2769.
- 44. T. Sugama, L. Kukacka, N. Carciello, N. Hocker. Cement and Concrete Res., 19 (1989) 857-867.
- 45. J. Schwar, P. Jahn, L. Wiedmann, A. Benninghoven. J. Vac. Sci. Technol. A, 9 (1991) 238-249.
- 46. M. Sosulnikov, Y.A. Teterin. J. Electron Spectrosc., 59 (1992) 111-126.
- 47. C. Plackowski, M.A. Hampton, A.V. Nguyen, W.J. Bruckard. Miner. Eng. 45 (2013) 59-66.
- 48. B. Zhou, Y. Wang, Y. Zuo. Appl. Surf. Sci., 357 (2015) 735-744.
- 49. X. Ouyang, X. Qiu, H. Lou, D. Yang. Ind. Eng. Chemi. Res., 45 (2006) 5716-5721.
- 50. L. Cizaire, J. Martin, T. Le Mogne, E. Gresser. Colloid Surface A., 238 (2004) 151-158.
- 51. M.J. Spencer, A. Hung, I.K. Snook, I. Yarovsky. Surf. Sci., 540 (2003) 420-430.
- 52. P. Błoński, A. Kiejna, J. Hafner. Surf. Sci., 590 (2005) 88-100.
- 53. J.A. Modi, K. Desai, S.R. Lokhandwala. Arab. J. Chem., 6(2013) 177-181.

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