Research Article

Evaluation of Corrosion Resistance of Corrosion Inhibitors for Concrete Structures by Electrochemical Testing in Saturated $\text{Ca}(\text{OH})_2$ Solutions with NaCl and Na_2SO_4

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Reinforcing steel maintains passivity in an alkaline concrete environment. However, the passive film on the steel can be destroyed as the concrete becomes acidic, which could induce the corrosion of reinforcing steel. Carbonates and sulfates destroy the concrete matrix and accelerate the penetration of hazardous ions, thereby deteriorating the structure. To alleviate the corrosion of internal reinforcing steel within concrete, corrosion inhibitors are most widely used. In this study, the effects of inorganic nitrite (lithium nitrite) and amino acid corrosion inhibitors (diethanolamine, methyl diethanolamine, and 4-aminobutyric) on corrosion resistance and the pH of the solution with various concentrations of Na_2SO_4 (0.89, 1.77 g/L) in saturated $\text{Ca}(\text{OH})_2$ that contained NaCl (0.98 g/L), which simulated the concrete environment, were investigated. The corrosion resistance of inhibitors was evaluated by corrosion potential, electrochemical impedance spectroscopy, and potentiodynamic techniques. The results indicated improvement of corrosion resistance by the addition of amino acid corrosion inhibitors. It was confirmed that the inhibitor adsorbed on the surface of the specimen and passivated to reduce the corrosion reaction. In addition, the 4-aminobutyric acid corrosion inhibitors had the corrosion protection efficiency of 67.87–77.80%, which is a higher value than that of the inorganic nitrite corrosion inhibitor (lithium nitrite: 69.36–75.93%) and other amino acid corrosion inhibitors (diethanolamine: 35.69–39.91%; methyl diethanolamine: 66.07–69.09%).

1. Introduction

The corrosion of steel reinforcements within concrete occurs as the passive films, formed on the steel surfaces in the alkaline environment of concrete, are destroyed. The passivity of reinforcing steel is promoted by the alkalinity of concrete, arising from the high pH of the concrete pore solution. However, protective oxides and passive films can be destroyed by the weakening of concrete and the ingress of harmful ions caused by the carbonation, sulfates attack, and acidic substances in industrial areas. The corrosion of steel can also be alleviated by using corrosion-resistant

steels, cathodic protection, fusion-bonded epoxy coatings, corrosion inhibitors, and admixtures. Among these methods, corrosion inhibitors are the most widely used, with high cost-effectiveness and convenient usage. Inhibitors prevent the onset of corrosion by increasing the concrete pH or by fixating harmful ions that can cause the corrosion of steel [1, 2]. Frequently used corrosion inhibitors include inorganic nitrites [3–5], inorganic phosphate [6] and molybdenum [7], monofluorophosphate that is applied to the surface of the concrete [8], and organic inhibitors, such as alkanolamine and amine groups [9–15].

Inorganic corrosion inhibitors are mostly nitrites, which have been used since the 1940s. Nitrite-based corrosion inhibitors are environmentally unfriendly with hazardous biological effects [16]. To replace nitrite-based corrosion inhibitors, organic-based inhibitors have been developed and used since the 1990s. Organic corrosion inhibitors show chelating effects with iron, which forms covalent bonds with lone pairs of electrons of the heteroatoms in the organic compound. The heteroatoms act as nucleophiles of iron, which is an electrophile. The lone pairs of the heteroatoms are donated to the vacant d -orbital of iron atoms, forming very strong covalent bonds. In this way, the organic inhibitor is adsorbed on the metal surface, yielding a very protective inert film [17, 18]. Organic inhibitors, especially amine- and alkanolamine-containing effectors, are frequently used as corrosion inhibitors owing to their high solubilities in aqueous solutions. Because of the functional groups of organic inhibitors, nitrogen and oxygen atoms are adsorbed on the metal surface with their lone pairs of electrons; the iron ions act as Lewis acids, accepting electrons from the nitrogen and oxygen donors. Very strong covalent bonds are formed between nitrogen/oxygen and iron metal, and considerable amounts of nitrogen and oxygen are adsorbed on the surface of the reinforcing steel [19]. Such organic inhibitors reduce or impede the corrosion of reinforcing steel through the adsorption of polar heteroatom groups, which form very thin protective layers. Therefore, inhibitors containing amino groups are commonly used to decrease the corrosion of reinforcing steel in contaminated concrete.

Before corrosion begins or at relatively low corrosion levels, amino alcohol inhibitors are more effective [20, 21]. Martin and Miksic reported that dimethylethanolamine blocks active sites and acts as a cathodic inhibitor. The oxygen absorbs electrons, thereby being reduced to OH^- and adsorbing on the anode. Amino alcohol inhibitors act more effectively than nitrite inhibitors, i.e., lithium nitrite, in both acceleration tests and saturated $\text{Ca}(\text{OH})_2$ solutions with different concentrations of chloride ions [22].

Studies about corrosion of reinforcing steel-simulating concrete environments using saturated $\text{Ca}(\text{OH})_2$ solutions have been reported elsewhere [23–25]. However, only a few corrosion studies have been performed for amine-based corrosion inhibitors in saturated $\text{Ca}(\text{OH})_2$ solutions bearing sulfate and chloride ions via electrochemical methods [26, 27]. Sulfate attack on concrete is a chemical deterioration mechanism where sulfate ions attack components of the cement paste to form expansive crystalline products called ettringite. Expansion due to ettringite formation results in stresses, and cracks develop in the concrete; therefore, it can accelerate corrosion by destroying the passive state of the rebar through lowering of the pH in the concrete pore environment [28].

In this study, the effects of inorganic nitrite and amino alcohol inhibitors on corrosion resistance and the pH of the solution with various concentrations of Na_2SO_4 in saturated $\text{Ca}(\text{OH})_2$ that contained NaCl, which simulated the concrete environment, were investigated. The

corrosion resistance of inhibitors was evaluated by various electrochemical tests, such as potential times, electrochemical impedance spectroscopy, and potentiodynamic techniques.

2. Materials and Methods

2.1. Materials. Commercially available inorganic nitrite corrosion inhibitor and amino acid corrosion inhibitors were used, and their physical properties are shown in Table 1. The pH of the saturated $\text{Ca}(\text{OH})_2$ solution was 12.8 at room temperature ($25^\circ\text{C} \pm 1^\circ\text{C}$). The pH was measured after mixing 0.98 g/L NaCl and various concentrations of Na_2SO_4 into the saturated $\text{Ca}(\text{OH})_2$. Since the pH adjustment is very delicate work in mixed solutions, the pH was set by the measurement after the preparation of solutions. The corrosion inhibitors of various concentrations were mixed in the $\text{Ca}(\text{OH})_2/\text{NaCl}/\text{Na}_2\text{SO}_4$ solutions.

Steel specimens of 16 mm in diameter were cut and placed in acid/alkali-resistant thermosetting resin. The mounted samples were polished with 180–1,200 μm sandpapers. The chemical composition of the steel specimens used in the test is shown in Table 2.

In this study, the effects of the inhibitors on corrosion resistance and the pH of the solution with various concentrations of chloride and sulfate ions, which simulated the concrete environment, were investigated. For this, the chloride ion concentration was fixed in the $\text{Ca}(\text{OH})_2$ solution, and by adjusting the admixing amount of sulfate ions, electrochemical tests were conducted to evaluate the performance of four different corrosion inhibitors. Table 3 shows the mixtures of each tested solution.

2.2. Electrochemical Testing. Electrochemical testing was conducted with a three-electrode system, in which the steel specimen acted as the work electrode (WE), platinum wire as the counterelectrode (CE), and silver chloride as the reference electrode (RE). The areas of the working electrodes were 0.78 cm^2 , held constant for all specimens. The steel specimens were exposed to the solutions, and the potential was stabilized with a potentiostat before the test.

Electrochemical impedance spectroscopy (EIS) was performed by changing the frequency of a 10 mV sinusoidal voltage from 0.1 Hz to 100 kHz. The DC polarization was performed from -0.3 V to $+0.3\text{ V}$ vs. the open-circuit potential with a scanning rate of 1 mV/s . The potentiostat was a VersaSTAT system (Princeton Applied Research, Oak Ridge, TN, USA), and data analysis was conducted by fitting the test data to the constant phase element (CPE) model using Metrohm Autolab Nova 1.10 software.

3. Results and Discussion

3.1. pH Measurement. Cement consists of calcium silicate phases termed C_2S and C_3S and calcium aluminate phases termed C_3A and C_4AF in cement chemistry notation. Among these compounds, C_2S (belite) and C_3S (alite)

TABLE 1: Physical properties of corrosion inhibitors.

Corrosion inhibitor	Specific gravity	pH	Value	
			Viscosity (cP)	Solid content (wt.%)
Lithium nitrite (LiNO_2)	1.052	12.84	8.0	75.0
Diethanolamine ($\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$)	1.097	12.21	10.0	90.0
Methyl diethanolamine ($\text{C}_5\text{H}_{13}\text{NO}_2$)	1.038	11.26	11.0	90.0
4-Aminobutyric acid ($\text{H}_2\text{N}(\text{CH}_2)_3\text{COOH}$)	1.110	7.99	9.0	80.0

TABLE 2: Chemical composition of steel specimens (wt.%).

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Sn	Fe
0.24	0.26	0.95	0.016	0.008	0.03	0.04	0.01	0.02	0.0005	Balance

TABLE 3: Representation of studied solutions.

Inhibitors	Concentration of NaCl (g/L)	Concentration of NaSO_4 (g/L)	Concentration of inhibitor (g/L)	Solution names
None	0.98	0.89	0.00	C0.98-S0.89
		1.77		C0.98-S1.77
Lithium nitrite (LiNO_2)	0.98	0.89	2.04	C0.98-S0.89-L2.04
		1.77		C0.98-S1.77-L2.04
Diethanolamine ($\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$)	0.98	0.89	0.51	C0.98-S0.89-D0.51
		1.77		C0.98-S1.77-D0.51
Methyl diethanolamine ($\text{C}_5\text{H}_{13}\text{NO}_2$)	0.98	0.89	0.50	C0.98-S0.89-M0.50
		1.77		C0.98-S1.77-M0.50
4-Aminobutyric acid ($\text{H}_2\text{N}(\text{CH}_2)_3\text{COOH}$)	0.98	0.89	0.38	C0.98-S0.89-A0.38
		1.77		C0.98-S1.77-A0.38

account for >70% of cement, and these two phases produce C-S-H and calcium hydroxide through hydration. In general, when the cement is completely hydrated, calcium hydroxides corresponding to ~20% of the prehydration weight are formed, thereby maintaining a high pH [29].

(1)

When sulfates penetrate the concrete, calcium hydroxide reacts with them to produce dihydrate gypsum. Through this process, an inflation pressure accumulates inside the concrete during the phase transition from hexagonal plates of calcium hydroxide to columns of dihydrate gypsum. Above a certain level of dihydrate gypsum generation, or upon localized concentration of dihydrate gypsum under continued sulfate attack, cracks form in the concrete. Furthermore, a pH decreases because the calcium hydroxide, which maintains the high pH of the concrete, is changed to plaster; therefore, damage is expected to occur in the passive film of reinforcing steel in the acidifying environment.

Figure 1 shows the measured pH for each aqueous solution. The pH of the $\text{Ca}(\text{OH})_2$ solution was 12.78; with admixing of Na_2SO_4 , the pH was dropped to ~11.7. Following the admixing of the corrosion inhibitors, pH

FIGURE 1: Results of pH measurement.

recovery was confirmed; the nitrite and amino acid corrosion inhibitors show the pH recovery functions of 6% and 3–6%, respectively. 4-Aminobutyric acid showed the lowest recovery rate of 3%. It is confirmed that the pH is reduced due to the reaction of calcium hydroxide with sulfate ion to produce dihydrate gypsum. It is considered that the pH can be recovered due to the immobilization reaction of sulfate ion by incorporating inhibitors.

3.2. Corrosion Potential. Corrosion potential was measured for the steel specimens in saturated $\text{Ca}(\text{OH})_2$ solutions containing different concentrations of NaCl, Na_2SO_4 , and corrosion inhibitors. The changes in the corrosion potential are shown in Figure 2, which provides information about the initiation of corrosion at the surface of the reinforcing steel.

FIGURE 2: Corrosion potential-time plots of steel specimens exposed in saturated Ca(OH)_2 solution with 0.98 g/L NaCl, different concentrations of Na_2SO_4 , and inhibitors.

The corrosion potential (absolute value) increases actively as the concentration of NaCl is increased. The steel surface is deteriorated more easily by NaCl in the Ca(OH)_2 solution, and corrosion of the steel specimen is increased [30]. Figure 2 shows a reduction in corrosion potential as the concentration of Na_2SO_4 increases because the reduction in pH could accelerate the corrosion at the surface of the steel. However, it is apparent that the corrosion potential increases when the inhibitors are mixed in the solution. This indicates the surface of the steel specimen is less active than the specimen without the inhibitor. The inhibitor could be adsorbed on the surface of the specimens and passivated them, thereby decreasing the corrosion reaction. The specimen with lithium nitrite shows similar corrosion potential to that without inhibitors at 1.77 g/L Na_2SO_4 . A similar trend is observed in the activation of the corrosion potential for diethanolamine and methyl diethanolamine. The specimen with 4-aminobutyric acid has the best corrosion resistance with the lowest corrosion potential regardless of the concentration of Na_2SO_4 .

3.3. Electrochemical Impedance Spectroscopy. In the saturated Ca(OH)_2 solutions containing 0.98 g/L NaCl and 0.89, 1.77 g/L Na_2SO_4 , EIS was conducted for steel specimens with various corrosion inhibitors. The size of the semicircular loop in the EIS is decreased as the concentration of sulfate ions increases (Figure 3). This can promote the corrosion of the reinforcing steel by increasing the concentration of anions in the solutions [31].

Figure 4 shows the impedance-frequency plots of reinforcing steels in the Ca(OH)_2 solutions mixed with various concentrations of Na_2SO_4 . As the concentration of sulfate ions is increased, the pH decreases and the resistance of the passive film decreases due to the film conductivity. Because chloride ions are present in the solution along with the sulfate ions, a reaction can occur at the activated region of the metal/solution interface [32]:

FIGURE 3: Nyquist plots of steel specimens exposed in saturated Ca(OH)_2 solution with 0.98 g/L NaCl and different concentrations of Na_2SO_4 .

FIGURE 4: Impedance-frequency bode plots of steel specimens exposed in saturated Ca(OH)_2 solution with 0.98 g/L NaCl and different concentrations of Na_2SO_4 .

For all reactions, it can be written as follows:

Fe(OH)_2 is unstable; by reacting with chloride ions in the solution, acidic ferrous chloride is formed:

FeCl_2 (acidic ferrous chloride) and OH^- at the anode and cathode parts induce the anodic dissolution of the reinforcing steel [33].

Reinforcing steel is in the passive state in alkaline concrete environments. When the concentration of chloride ions increases or the pH decreases below 12.5, the passivity can be destroyed. The pH can be decreased by the carbonation of concrete via acidic substances present in solution. This reduction in pH causes destruction of the passive film, and in the presence of anions such as Cl^- , the steel rebars produce corrosion products by the same reaction as in equations (4) and (5). In this study, the sodium sulfate admixed in the saturated $\text{Ca}(\text{OH})_2$ solution decreases the pH; because chloride ions are present, the passive film on the steel specimen surface becomes hydrated.

Nyquist plots and impedance-frequency bode plots of the steel specimens in the solution with various inhibitors are shown in Figures 5 and 6, respectively. Figure 5 shows the Nyquist plots; when the concentration of corrosion inhibitor is increased, the size of the semicircular loop increases. It was confirmed that the capacitance increases with the incorporation of the corrosion inhibitor. This result indicated that the corrosion inhibitor is adsorbed on the surface of the steel specimen to form a protective inactive film. The concentration of the inhibitor is important in strengthening the passive film. In this process, the corrosion inhibitor provides a passive film and homogeneity. This result implies that the inhibitor substitutes chloride ions on the steel surface and forms a protective inert film [34]. Figure 6 shows the total impedance at a low frequency (0.1 Hz). The impedance values are higher in the presence of inhibitors compared to that without an inhibitor, and the highest impedance value occurs with 4-aminobutyric acid. The corrosion inhibitor is adsorbed on the steel surface, thereby homogenizing the passive film. It is confirmed that the corrosion inhibition performance of 4-aminobutyric acid is the highest. Figure 7 shows a graph of the phase frequencies in the electrochemical corrosion measurements of each aqueous solution.

In the case of 0.98 g/L NaCl and 1.77 g/L Na_2SO_4 mixed in the saturated $\text{Ca}(\text{OH})_2$ solutions, the inhibitor effects are confirmed with 0.6 mol lithium nitrite, diethanolamine, methyl diethanolamine, and 4-aminobutyric acid, as shown in Figures 8 and 9. The semicircle loop sizes for the steel specimens are increased in the $\text{Ca}(\text{OH})_2$ solution mixed with 0.6 mol inhibitor compared to the case of 1.2 mol inhibitor (Figure 8). This is because of the capacitive characteristic of the passive film formed by the inhibitor. The passive film on the steel specimen becomes weaker in the $\text{Ca}(\text{OH})_2$ solution containing 1.77 g/L Na_2SO_4 compared to that containing 0.89 g/L Na_2SO_4 . With this result, it is determined that not only the decrease of pH but also the concentration increase of sulfate ions hinders the passivating effect of the inhibitor. Figure 10 shows a graph of the phase-frequencies in the electrochemical corrosion measurements of each aqueous solution.

Compared to the case without an inhibitor, the increase of the semicircle loop is larger with the organic diethanolamine, methyl diethanolamine, and 4-aminobutyric

FIGURE 5: Nyquist plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 0.89 g/L Na_2SO_4 , and inhibitors.

FIGURE 6: Impedance-frequency bode plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 0.89 g/L Na_2SO_4 , and inhibitors.

acid corrosion inhibitors than that with the inorganic lithium nitrite corrosion inhibitor. With equal concentrations of chloride ions, the loop increase of methyl diethanolamine is high for low concentrations of sulfate ions and that of 4-aminobutyric acid is high for high concentrations of sulfate ions. In Figure 9, it can be confirmed that the impedance value is decreased more at the low frequency (0.1 Hz) in the aqueous solution containing a high concentration of sulfate ions because of the hindrance of sulfate ions, compared to the case of low concentration. With 4-aminobutyric acid, the high impedance value is also maintained in the aqueous solution bearing highly concentrated sulfate ions.

For 0.98 g/L NaCl and 0.89 or 1.77 g/L Na_2SO_4 mixed in the saturated $\text{Ca}(\text{OH})_2$ solution, polarization resistance of the steel specimen was measured following the addition of the corrosion inhibitors. The polarization resistance

FIGURE 7: Phase-frequency bode plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 0.89 g/L Na_2SO_4 , and inhibitors.

FIGURE 8: Nyquist plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 1.77 g/L Na_2SO_4 , and inhibitors.

decreases as the conductivity of the solution is increased. An increase in the conductivity of the solution, i.e., distribution of anions such as chloride ions that destroy the passive film, induces localized corrosion of the steel. Table 4 shows the polarization resistance values for each solution. According to the admixing of the corrosion inhibitor, the polarization resistance increases, and as the mixing amount of sodium sulfate increases, the polarization resistance decreases. In the case of 0.89 g/L Na_2SO_4 , the corrosion inhibitor becomes homogenized, thereby strengthening the inert characteristic of the film, but at a high concentration (1.77 g/L) of Na_2SO_4 , the formation of the inert layer between the steel interface and solution is hindered.

The efficiency of each corrosion inhibitor can be calculated with the following equation [35]:

FIGURE 9: Impedance-frequency bode plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 1.77 g/L Na_2SO_4 , and inhibitors.

$$\eta(\%) = \frac{R_{\text{pore}} - R_{\text{pore}}^0}{R_{\text{pore}}} \times 100, \quad (6)$$

where R_{pore} and R_{pore}^0 are the polarization resistance with and without the inhibitor, respectively. As the amount of Na_2SO_4 increases, the efficiency of the corrosion inhibitor decreases. In the solution mixed with a low concentration of 0.89 g/L Na_2SO_4 , the lithium nitrite inhibitor had 69.36% efficiency, diethanolamine inhibitor 39.91%, methyl diethanolamine inhibitor 69.09%, and 4-aminobutyric acid 77.80%. Furthermore, in the solution mixed with a high concentration of 1.77 g/L Na_2SO_4 , the lithium nitrite inhibitor had 75.93% efficiency, diethanolamine inhibitor 35.69%, methyl diethanolamine inhibitor 66.07%, and 4-aminobutyric acid 67.87%. Overall, the 4-aminobutyric acid inhibitor has the highest efficiency.

3.4. Potentiodynamic Test. Potentiodynamic tests were performed for steel specimens with various corrosion inhibitors in the saturated $\text{Ca}(\text{OH})_2$ solutions containing 0.98 g/L NaCl and 0.89 or 1.77 g/L Na_2SO_4 . Figure 11 shows the potentiodynamic plots according to the admixed amount of sulfate ions. When chloride ions are present, pitting corrosion is induced on the steel specimen in the saturated $\text{Ca}(\text{OH})_2$ solution; as the sulfate ions are admixed, the corrosion current density (I_{corr}) increases and the corrosion potential (E_{corr}) is changed more significantly.

Figure 12 shows the potentiodynamic plots for the cases of 0.98 g/L NaCl and 0.89 g/L Na_2SO_4 mixed in the saturated $\text{Ca}(\text{OH})_2$ solutions. In Figure 12, the corrosion current density decreases and the corrosion potential moves in the positive direction with the addition of corrosion inhibitor. This result implies that the corrosion inhibitor, which has adsorption characteristics, exists on the steel specimen surface, thereby preventing reactions between iron ions and anions that cause corrosion. The current densities of the organic inhibitors, i.e., diethanolamine, methyl

FIGURE 10: Phase-frequency bode plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 1.77 g/L Na_2SO_4 , and inhibitors.

TABLE 4: Polarization resistance of steel specimens and Efficiency of inhibitors exposed in saturated $\text{Ca}(\text{OH})_2$ solution 0.98 g/L NaCl and different concentrations of Na_2SO_4 .

Inhibitors	Concentration of NaCl (g/L)	Concentration of NaSO ₄ (g/L)	Concentration of inhibitor (g/L)	Polarization resistance, R_{pore} ($\Omega\cdot\text{cm}^2$)	Efficiency, η (%)
None	0.98	0.89	0.00	4356	
		1.77		3227	
0.89		2.04	14219	69.36	
1.77			13407	75.93	
0.89		0.51	7249	39.91	
1.77			5018	35.69	
0.89		0.50	14093	69.09	
1.77			9512	66.07	
0.89		0.38	19623	77.80	
1.77			10044	67.87	

(a)

(b)

FIGURE 11: Continued.

(c)

FIGURE 11: Potentiodynamic plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl and different concentrations of Na_2SO_4 . (a) C0.98-S0; (b) C0.98-S0.89; (c) C0.98-S1.77.

(a)

(b)

(c)

(d)

FIGURE 12: Potentiodynamic plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 0.89 g/L Na_2SO_4 , and inhibitors. (a) C0.98-S0.89-L2.04; (b) C0.98-S0.89-D0.51; (c) C0.98-S0.89-M0.50; (d) C0.98-S0.89-A0.38.

FIGURE 13: Potentiodynamic plots of steel specimens exposed in saturated $\text{Ca}(\text{OH})_2$ solution with 0.98 g/L NaCl, 1.77 g/L Na_2SO_4 , and inhibitors, (a) C0.98-S1.77-L2.04; (b) C0.98-S1.77-D0.51; (c) C0.98-S1.77-M0.50; (d) C0.98-S1.77-A0.38.

diethanolamine, and 4-aminobutyric acid, are lower than that of the inorganic inhibitor, i.e., lithium nitrite; in the aqueous solution containing 4-aminobutyric acid, the current density is the lowest and the corrosion potential is the most enhanced.

Figure 13 shows the potentiodynamic plots for the case of 0.98 g/L NaCl and 1.77 g/L Na_2SO_4 mixed in the saturated $\text{Ca}(\text{OH})_2$ solution. Compared to Figure 12, the current density is increased and the corrosion potential is decreased due to the increased concentration of sulfate ions. Furthermore, it is confirmed that several pitting-type corrosions can occur at the lower corrosion potential. Alleviation of the corrosion is also confirmed in the aqueous solution, in which the corrosion possibility becomes high with the increase of sulfate ions. In terms of the current density and corrosion

potential, 4-aminobutyric acid has the most corrosion inhibition ability among the organic inhibitors.

The principle of corrosion inhibiting is that the functional groups of the inhibitor react with iron ions, thereby forming a protective film. For inorganic lithium nitrite, the nitrite reacts with the iron ions and forms a passive film. For organic diethanolamine and methyl diethanolamine, containing hydroxyl and amine groups, they act as nucleophiles and react with the metal. Afterwards, the diethanolamine and methyl diethanolamine inhibitors form very thin and protective oxide layers on the surfaces of reinforcing steels. Furthermore, 4-aminobutyric acid contains carboxyl and amine groups; like the other organic inhibitors, it acts as a nucleophile, thereby donating to the vacant d -orbitals of iron atoms and forming coordinated covalent bonds. Therefore, the inhibitor is

adsorbed on the steel surface and forms a uniform corrosion-preventing layer.

4. Conclusions

This study evaluated the performances of inorganic nitrite and amino acid corrosion inhibitors and their effects on the pH with various concentrations of Na_2SO_4 in saturated $\text{Ca}(\text{OH})_2$ solutions that contained NaCl, which simulated the concrete environment. The results are as follows:

- (1) In the saturated $\text{Ca}(\text{OH})_2$ solution bearing a certain concentration of NaCl, the electrochemical corrosion tendency of the steel specimen changed depending on the concentration of Na_2SO_4
- (2) In the $\text{Ca}(\text{OH})_2$ solution mixed with NaCl and Na_2SO_4 , the lithium nitrite inhibitor had a corrosion prevention efficiency of 69.36–75.93%, diethanolamine 35.69–39.91%, methyl diethanolamine 66.07–69.09%, and 4-aminobutyric acid 67.87–77.80%
- (3) In the $\text{Ca}(\text{OH})_2$ solution mixed with NaCl, as the Na_2SO_4 concentration increased, the corrosion prevention efficiency decreased
- (4) EIS studies confirmed the corrosion resistance of the inhibitors with different concentrations of NaCl and Na_2SO_4
- (5) The results of potentiodynamic tests with the inhibitors showed the passivation behavior of reinforcing steel in the $\text{Ca}(\text{OH})_2$ solution in which chloride and sulfate ions were present

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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