

Effects of Inhibitors on Corrosion Resistance of Steel in CaCl₂ Solution Based on Response Surface Analysis

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(Received June 15, 2021; Revised June 24, 2021; Accepted June 24, 2021)

Effects of corrosion inhibitors (i.e., sodium nitrite, sodium hexametaphosphate, trimethylamine (TEA), sugar, and urea) on the corrosion resistance of carbon steel in CaCl₂ solution were investigated. The test solution was designed with response surface methodology of design of experiments (DOE) in the range of 0 ~ 50 ppm for NaNO₂, 0 ~ 200 ppm for (NaPO₃)₆, 0 ~ 2000 ppm for TEA, 0 ~ 3000 ppm for sugar, 0 ~ 200 ppm for urea with 3 wt% CaCl₂. The corrosion potential and the corrosion rate were measured with potentiodynamic polarization tests and analyzed statistically to find main effects of inhibitor concentrations and interactions between them. As a result, hexametaphosphate was the most effective compound in reducing the corrosion rate. Sugar also reduced the corrosion rate significantly possibly because it covered the surface effectively with a high molecular weight. The inhibiting action of sugar was found to be enhanced by adding trimethylamine into the solution. Nevertheless, trimethylamine did not appear to be effective in inhibiting corrosion by itself. However, urea and sodium nitrite showed almost no inhibition on corrosion resistance of steel.

Keywords: Corrosion, Design of Experiment (DOE), Corrosion inhibitor, Steel, Chloride

1. Introduction

Deicing agents are widely used in the winter season with heavy snow. CaCl₂, NaCl, and MgCl₂ are the major ingredient of deicing agents which lower the melting point of water and provide an exothermic reaction to melt the ice on the ground. However, the chloride ions cause corrosion of automobiles and steels in the concrete. The easiest way to reduce the corrosivity of deicing agents is to add corrosion inhibitors into the chlorides. Nitrites, phosphates, amines, sugars are commonly employed as corrosion inhibiting additives in the deicing agents. They can promote passivity or suppress the passivity breakdown by adsorbing on the surface [1-7]. Nitrite promotes the formation of the passive film composed of α - or γ -FeOOH on steels and lowers the oxygen concentration resulting in a reduction of the corrosion rate [1-3]. Hexametaphosphate is known as an anodic inhibitor that cleans the surface and promotes passivity, but it is also known to accelerate oxidation when overdosed [5]. Various organic compounds

are adsorption type inhibitors that suppress the activity of Cl⁻ ions on the surface [5].

Industrial companies need their own recipes of additives to optimize the corrosivity, deicing performance, and also costs. There is a variety of corrosion inhibitors possibly used, so we need to employ an efficient research method to find the optimum composition. The Design of Experiments (DOE) has high advantages for such a situation [6]. Most of all, it reduces the number of experiments greatly. If we want to examine the effects of 5 kinds of inhibitors on the corrosion rate, $3^5 = 243$ runs of experiments should be done when we set the concentration of each inhibitor as high, moderate, and low levels. However DOE provides quantitative information about the effect of each inhibitor by a statistical analysis of only 32 ~ 54 experiments, depending on the specific methodology. Further, the interactions between inhibitors such as a synergy or an interference can be known. The DOE has been used to design materials composition or process. The Response Surface Methodology (RSM), which is one type of the DOE, is reported to be used successfully in examining the effects of various elements or compounds

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on the material performance [7-9]. The RSM presumes the response as a curved surface determined by a regression function of independent variables. When the response surface is plotted in a curve, a contour, or a 3-dimensional graph, we can easily recognize the trends of the response in relation to the parameters and the optimum points.

In this work, we employed RSM to investigate the effects of corrosion inhibitors which are sodium nitrite, sodium hexametaphosphate, trimethylamine, sugar, and urea in CaCl_2 solutions. The electrochemical corrosion behavior of steel was measured and statistically analyzed.

2. Materials and Methods

The composition of experimental solutions was designed by Central Composite Design (CCD) scheme of RSM. It is suitably employed when we want to know how the factors influence the response value, to find the factor values that satisfy the specific condition, and to optimize the response by controlling the factors. In CCD, the factors are controlled as shown in Fig. 1, schematically. The coded value of factors are represented as -1 (low), 0 (center), and +1 (high). Therefore the experimental runs for 2 factors are as shown as (0, 0), (1, -1), (-1, 1), (1, 1), (-1, -1), (0, 1), (0, -1), (1, 0), (-1, 0). The center point is tested repetitively for statistical stability.

Regression model with k factors can be written as follows when secondary function was assumed;

$$y = \sum_{i=0}^k \beta_i X_i + \sum_{i,j} \beta_{ij} X_i X_j + \epsilon \quad (1)$$

where X is the factor value, y is the response value, β is the coefficient for the terms, ϵ is a constant. In this study, X is the concentration of each inhibitor and y is the corrosion rate or corrosion potential. The coefficients in the linear terms will show how strongly each inhibitor affects the corrosion behavior. The coefficients of secondary terms indicate the interactions between the inhibitors.

The compositions of experimental solutions design by CCD is shown in Table 1. The concentrations of inhibitors were in the range of 0 ~ 50 ppm NaNO_2 , 0 ~ 200 ppm $(\text{NaPO}_3)_6$, 0 ~ 2000 ppm TEA, 0 ~ 3000 ppm sugar, 0 ~ 200 ppm urea. The potentiodynamic polarization curves of steel were measured in each solution. The corrosion rate and corrosion potential were determined by Tafel extrapolation and analyzed by Minitab 18 software.

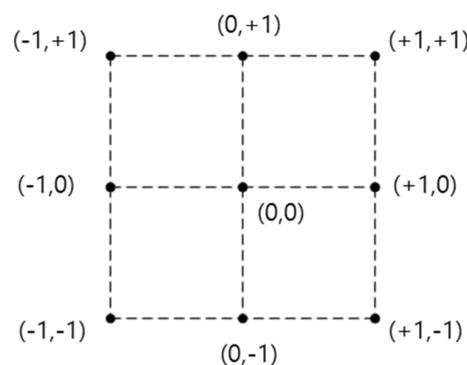


Fig. 1. Schematic representation of central composite design with 2 factors

Table 1. Composition of test solutions designed by Response Surface Methodology in the range of 0 ~ 50 ppm NaNO_2 , 0 ~ 200 ppm $(\text{NaPO}_3)_6$, 0 ~ 2000 ppm TEA, 0 ~ 3000 ppm sugar, 0 ~ 200 ppm urea

Sample no.	CaCl_2 (wt%)	NaNO_2 (ppm)	$(\text{NaPO}_3)_6$ (ppm)	TEA (ppm)	Sugar (ppm)	Urea (ppm)
1	3	25	100	1000	1500	100
2	3	25	100	1000	1500	100
3	3	0	200	2000	0	200
4	3	25	100	2000	1500	100
5	3	50	100	1000	1500	100
6	3	50	0	0	0	200
7	3	25	100	1000	1500	100
8	3	0	0	0	3000	0
9	3	25	0	1000	1500	100

Table 1. (Continued) Composition of test solutions designed by Response Surface Methodology in the range of 0 ~ 50 ppm NaNO₂, 0 ~ 200 ppm (NaPO₃)₆, 0 ~ 2000 ppm TEA, 0 ~ 3000 ppm sugar, 0 ~ 200 ppm urea

Sample no.	CaCl ₂ (wt%)	NaNO ₂ (ppm)	(NaPO ₃) ₆ (ppm)	TEA (ppm)	Sugar (ppm)	Urea (ppm)
10	3	50	200	0	0	0
11	3	50	0	2000	3000	200
12	3	25	100	1000	0	100
13	3	25	100	1000	1500	100
14	3	0	0	0	0	0
15	3	0	0	2000	0	200
16	3	50	200	2000	0	200
17	3	50	0	0	3000	200
18	3	50	200	2000	0	0
19	3	50	0	2000	3000	0
20	3	50	200	0	3000	0
21	3	25	100	1000	1500	100
22	3	0	200	2000	0	0
23	3	25	100	1000	1500	100
24	3	0	200	0	0	0
25	3	0	200	0	3000	200
26	3	0	200	0	0	200
27	3	0	200	0	3000	0
28	3	0	0	2000	0	0
29	3	50	0	0	0	0
30	3	25	100	1000	3000	100
31	3	25	100	1000	1500	100
32	3	0	100	1000	1500	100
33	3	0	0	0	0	200
34	3	0	0	2000	3000	200
35	3	50	200	2000	3000	200
36	3	25	100	1000	1500	100
37	3	50	0	2000	0	200
38	3	50	200	0	0	200
39	3	25	100	0	1500	100
40	3	25	100	1000	1500	100
41	3	25	100	1000	1500	200
42	3	50	0	0	3000	0
43	3	0	200	2000	3000	0
44	3	0	200	2000	3000	200
45	3	50	200	0	3000	200
46	3	50	0	2000	0	0
47	3	25	200	1000	1500	100
48	3	50	200	2000	3000	0
49	3	0	0	2000	3000	0
50	3	25	100	1000	1500	100
51	3	25	100	1000	1500	0
52	3	0	0	0	3000	200

Table 2. Nominal composition of the SPCC steel by KS D 3512 standard, used as the specimen in this study

Element	S	P	Mn	C	Fe
Content (wt%)	< 0.05	< 0.05	< 0.6	< 0.15	Balance

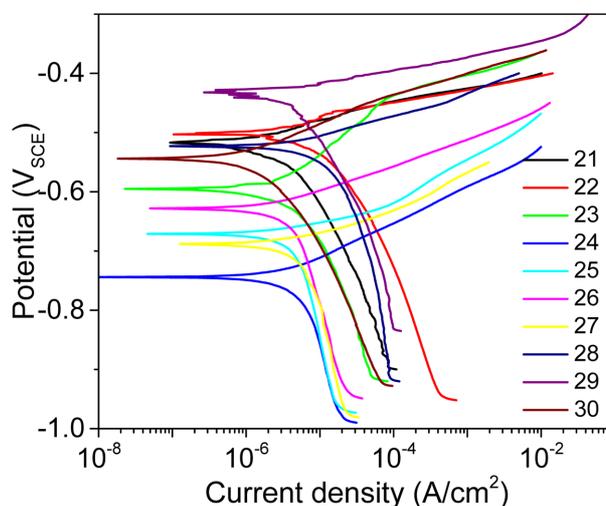
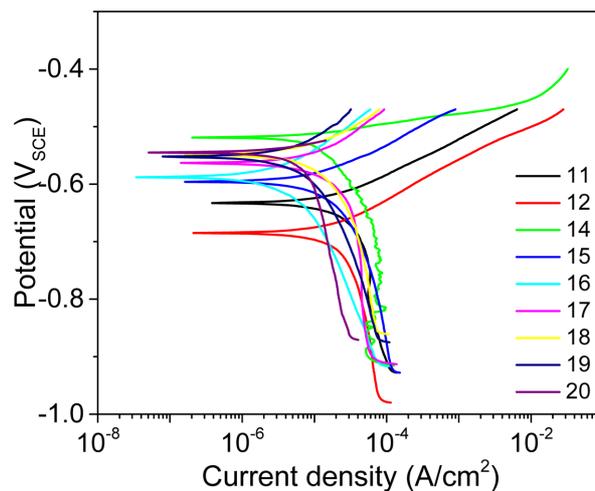
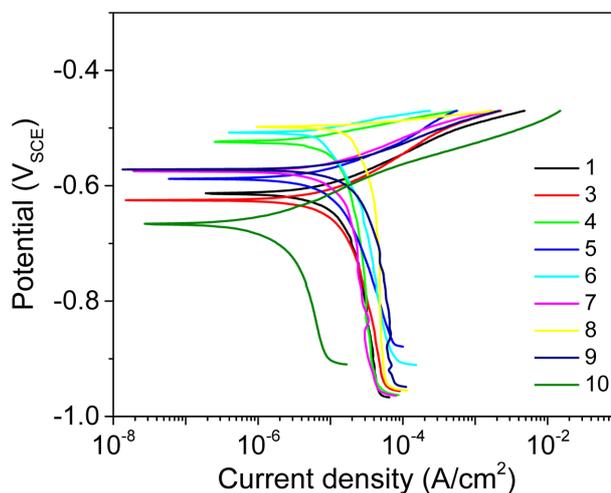
The polarization tests were performed with 3-electrodes electrochemical cell equipped with a working electrode made of cold-rolled carbon steel (Table 2), a counter electrode of platinum, and a SCE (saturated calomel electrode) as reference. The surface of the working electrode was ground up to 2000 grit by SiC paper and masked, leaving the exposed area of 0.05 ~ 0.1 cm². The test solutions were kept at a temperature of 25 ± 1 °C and were not deaerated. The open circuit potential was monitored during 1800 s and the potential was increased at a rate of 0.5 mV/s from -0.3 V with respect to the open circuit potential.

3. Results and Discussion

The polarization curves of steel measured in solutions as shown in Table 1 is presented in Fig. 2. Active dissolution or localized corrosion were observed for the most of samples, without a stable passivity region. The corrosion potential and corrosion rate were determined from the polarization curves and listed in Table 3. The corrosion potential was -0.44 ~ -0.74 V_{SCE} and the corrosion rate was 7.3 × 10⁻⁸ ~ 1.2 × 10⁻⁵ A/cm². The inhibition efficiency was calculated with respect to the corrosion rate of no. 14, which has no inhibitor, based on the following equation:

$$\text{inhibition efficiency} = (i_{\text{corr, inhibited}} - i_{\text{corr, uninhibited}}) / i_{\text{corr, inhibited}} \quad (2)$$

The highest inhibition efficiency from the experiments was 99% and was obtained using the solution no. 40 (Table 3). It contains the middle concentration of all additives (Table 2). No. 31 showed inhibition efficiency of 97% and it has the same composition with no. 40. Actually, ten test solutions, i.e., nos. 1, 2, 7, 13, 21, 23, 31, 36, 40, and 50, have the same compositions for the center point repetition of RSM. However the corrosion rate of them extends over large range, showing that the experimental data has high noise probably due to the uncontrolled oxygen concentration in the solution. The statistical analysis using DOE is highly useful in deriving



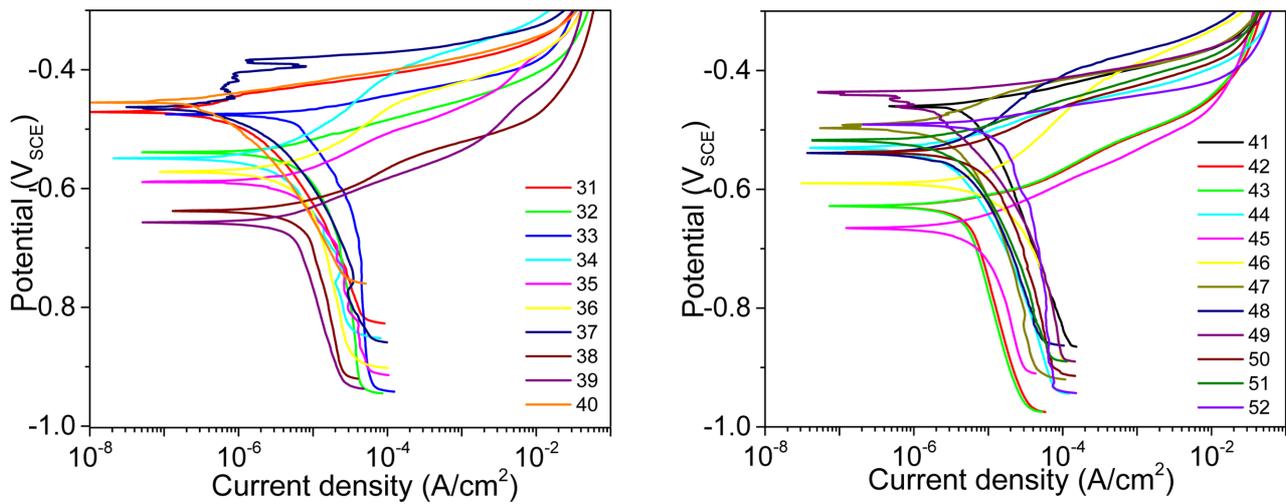


Fig. 2. (Continued) Potentiodynamic polarization curves of SPCC/S/B steel in the CaCl₂ solutions with the compositions as listed in Table 1

a meaningful trends instead of choosing wrong individual samples in this situation. Further in Table 3, the corrosion rate of 90% reduced by only 50 ppm of NaNO₂ (no. 29). By adding 200 ppm of (NaPO₃)₆ to the composition of no. 29, the inhibition efficiency increased slightly to 93%

(no. 10). Nos. 43 and 44 has similar composition except urea (0 ppm NaNO₂, 200 ppm (NaPO₃)₆, 2000 ppm TEA, 3000 ppm sugar, and 0 ~ 200 ppm urea) and they showed high inhibition efficiency of 86 ~ 88%. It is hard to find a regularity in these findings.

Table 3. E_{corr} and i_{corr} of SPCC/S/B steel in the CaCl₂ solutions with the compositions as listed in Table 1

No.	E _{corr} (V _{SCE})	i _{corr} (A/cm ²)	Inhibition efficiency (%)	No.	E _{corr} (V _{SCE})	i _{corr} (A/cm ²)	Inhibition efficiency (%)
1	-0.61	5.56 × 10 ⁻⁶	20%	27	-0.68	2.36 × 10 ⁻⁶	67%
2	-0.62	1.16 × 10 ⁻⁵	-64%	28	-0.52	5.26 × 10 ⁻⁶	26%
3	-0.62	1.63 × 10 ⁻⁶	77%	29	-0.43	7.30 × 10 ⁻⁷	90%
4	-0.52	3.30 × 10 ⁻⁶	53%	30	-0.54	2.25 × 10 ⁻⁶	68%
5	-0.58	4.21 × 10 ⁻⁶	40%	31	-0.46	2.40 × 10 ⁻⁷	97%
6	-0.5	4.26 × 10 ⁻⁶	40%	32	-0.53	1.58 × 10 ⁻⁶	78%
7	-0.57	2.43 × 10 ⁻⁶	66%	33	-0.47	6.54 × 10 ⁻⁶	7%
8	-0.49	1.17 × 10 ⁻⁵	-65%	34	-0.59	3.22 × 10 ⁻⁶	54%
9	-0.57	3.64 × 10 ⁻⁶	49%	35	-0.54	2.42 × 10 ⁻⁶	66%
10	-0.66	4.83 × 10 ⁻⁷	93%	36	-0.57	1.74 × 10 ⁻⁶	75%
11	-0.63	9.82 × 10 ⁻⁶	-39%	37	-0.46	1.65 × 10 ⁻⁶	77%
12	-0.68	6.00 × 10 ⁻⁶	15%	38	-0.64	6.77 × 10 ⁻⁶	4%
13	-0.51	1.59 × 10 ⁻⁶	78%	39	-0.65	3.02 × 10 ⁻⁶	57%
14	-0.51	7.07 × 10 ⁻⁶	0%	40	-0.45	7.33 × 10 ⁻⁸	99%
15	-0.59	4.00 × 10 ⁻⁶	43%	41	-0.45	7.98 × 10 ⁻⁶	-13%
16	-0.58	1.24 × 10 ⁻⁶	82%	42	-0.63	2.01 × 10 ⁻⁶	72%
17	-0.56	8.31 × 10 ⁻⁶	-18%	43	-0.51	8.17 × 10 ⁻⁷	88%
18	-0.54	2.78 × 10 ⁻⁶	61%	44	-0.53	9.83 × 10 ⁻⁷	86%

Table 3. (Continued) E_{corr} and i_{corr} of SPCC/S/B steel in the CaCl_2 solutions with the compositions as listed in Table 1

No.	E_{corr} (V_{SCE})	i_{corr} (A/cm^2)	Inhibition efficiency (%)	No.	E_{corr} (V_{SCE})	i_{corr} (A/cm^2)	Inhibition efficiency (%)
19	-0.55	5.64×10^{-6}	20%	45	-0.66	5.50×10^{-6}	22%
20	-0.54	1.89×10^{-6}	73%	46	-0.59	8.63×10^{-6}	-22%
21	-0.51	6.97×10^{-6}	1%	47	-0.48	3.11×10^{-6}	56%
22	-0.50	1.69×10^{-6}	76%	48	-0.54	1.57×10^{-6}	78%
23	-0.59	1.33×10^{-6}	81%	49	-0.44	4.54×10^{-6}	36%
24	-0.74	3.29×10^{-6}	53%	50	-0.53	2.38×10^{-6}	66%
25	-0.67	2.15×10^{-6}	70%	51	-0.51	1.21×10^{-5}	-71%
26	-0.62	1.82×10^{-6}	74%	52	-0.47	7.98×10^{-6}	-13%

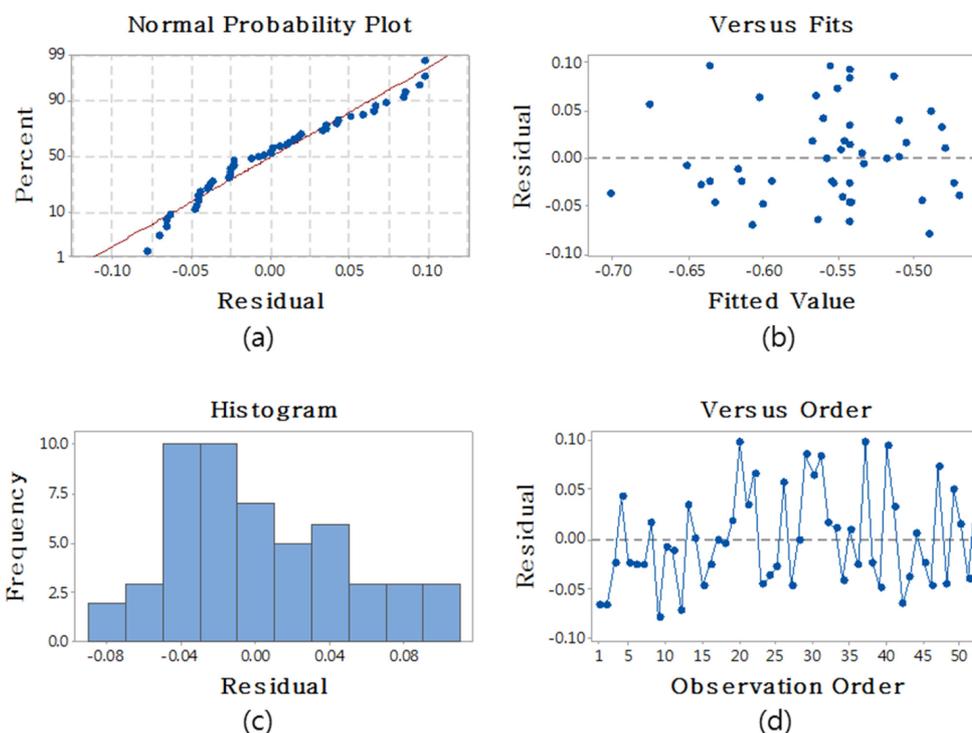
**Fig. 3. Residual plots for E_{corr} of SPCC/S/B steel in the CaCl_2 solutions with the compositions as listed in Table 1**

Fig. 3 shows the residual plots for corrosion potential (E_{corr}). The residuals do not depend apparently on the fitted value (Fig. 3b) and on the observation order (Fig. 3d). However, the normal probability plot (Fig. 3a) and the histogram were out of normal distribution (Fig. 3c). In addition, the R^2 value was as low as 55 % and two outliers were detected (Table 4). This result means that the regression result is not satisfactory. The samples no. 20 and no. 37 leave away largely from the regression. These outliers, caused possibly by experimental errors, could make the regression unacceptable.

Table 4. Outliers of E_{corr} determined from the statistical analysis of Fig. 3

No.	E_{corr}	Fitted value	Residual	Standardized residual
20	-0.5400	-0.6370	0.0970	2.19
37	-0.4600	-0.5573	0.0973	2.20

The residual plots for the corrosion rate (i_{corr}), shown in Fig. 4, does not fit into the normal distribution. The normal probability plot (Fig. 4a) appears linear but the Figs. 4b ~ d show that the residual is not distributed

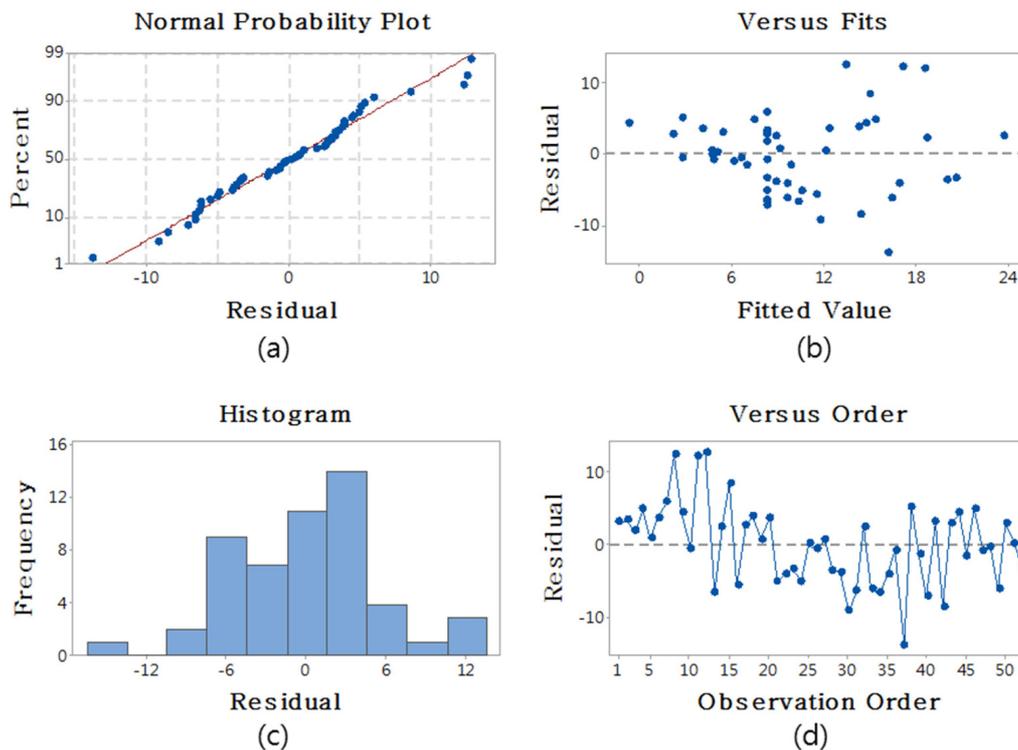


Fig. 4. Residual plots for i_{corr} of SPCC/S/B steel in the CaCl₂ solutions with the compositions as listed in Table 1

Table 5. Outliers of i_{corr} determined from the statistical analysis of Fig. 3

No.	i_{corr}	Fitted value	Residual	Standardized residual
8	29.40	17.03	12.37	2.44
11	30.60	18.47	12.13	2.39
12	26.00	13.37	12.63	2.44
37	2.29	16.05	-13.76	-2.71

randomly. The R^2 was 47% and four outliers were listed (Table 5).

Fig. 5, Fig. 6, Table 6, and Table 7 show the regression results without the outliers found the former analysis, i.e., no. 8, 11, 12, 20, and 37. The residuals became closer to the normal distribution (Figs. 5 and 6) and R^2 s were increased to 68 ~ 69%. In Table 6, the P-values of $(NaPO_3)_6$, $(NaPO_3)_6*TEA$, and $TEA*urea$ are lower than 0.05. Researchers usually consider that the terms with $P < 0.05$ meaningful but do not exclude the other terms completely. Especially for the case such as TEA and urea, it should be taken in account because it is meaningful for the second order terms. As for the i_{corr} (Table 7), the terms of $(NaPO_3)_6$, sugar, and $TEA*sugar$ have P-values less than 0.05. It is thought that $(NaPO_3)_6$, TEA, urea, and sugar

Table 6. Regression results for $E_{corr}(V_{SCE})$ excluding outliers shown in Table 4 and Table 5

Term	Coefficient	P-value
Constant	-0.5359	0.000
NaNO ₂	-0.0154	0.144
$(NaPO_3)_6$	-0.0292	0.008
TEA	0.0202	0.063
Sugar	-0.0035	0.733
Urea	-0.0054	0.610
NaNO ₂ *NaNO ₂	-0.0255	0.463
$(NaPO_3)_6*(NaPO_3)_6$	0.0045	0.896
TEA*TEA	-0.0555	0.117
sugar*sugar	-0.0134	0.762
urea*urea	0.0495	0.160
NaNO ₂ * $(NaPO_3)_6$	0.0132	0.233
NaNO ₂ *TEA	-0.0068	0.528
NaNO ₂ *sugar	-0.0134	0.200
NaNO ₂ *urea	0.0007	0.947
$(NaPO_3)_6*TEA$	0.0480	0.000
$(NaPO_3)_6*sugar$	0.0060	0.563
$(NaPO_3)_6*urea$	0.0105	0.334
TEA*sugar	0.0188	0.079
TEA*urea	-0.0278	0.013
sugar*urea	0.0038	0.712

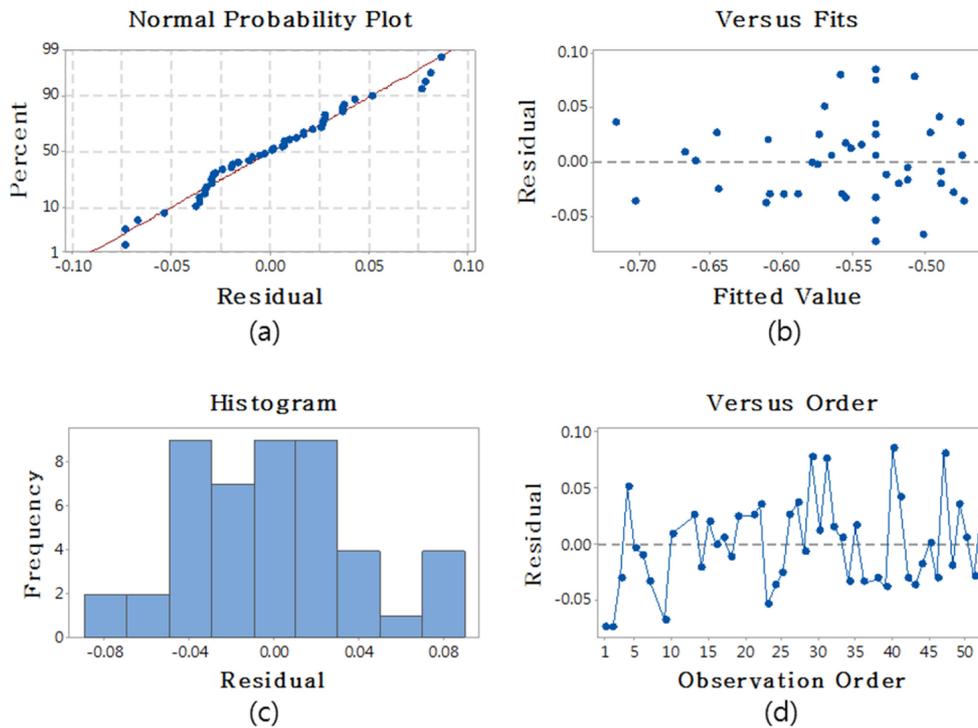


Fig. 5. Residual plots for E_{corr} excluding outliers listed in Table 4 and Table 5

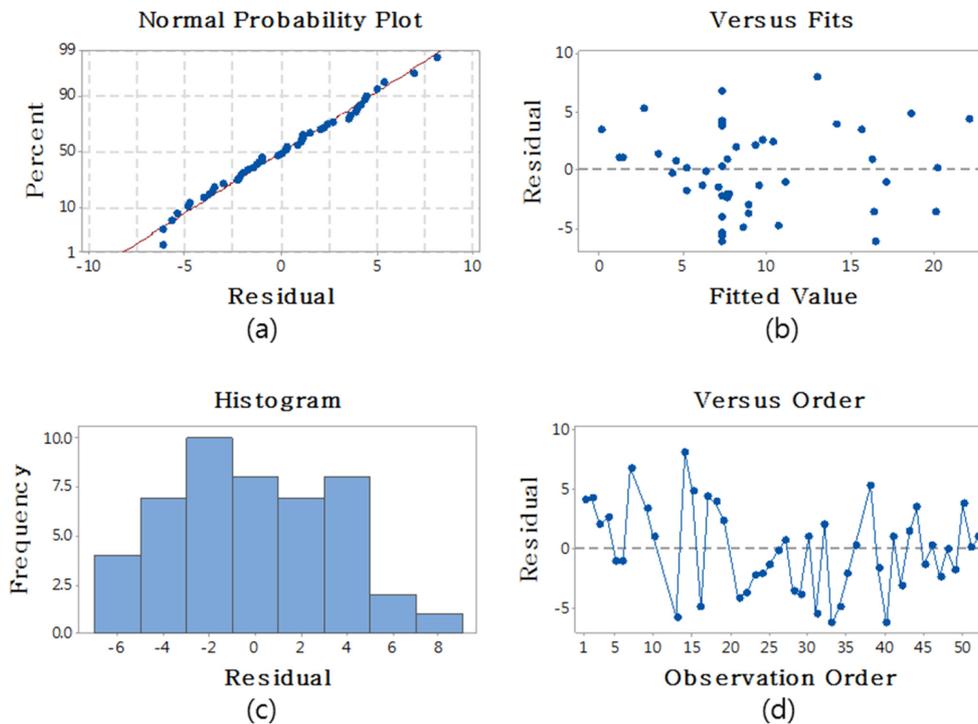


Fig. 6. Residual plots for i_{corr} excluding outliers listed in Table 4 and Table 5

are more influential to corrosion behavior than NaNO_2 .

The main effects and interactions of additives are analyzed and presented in Fig. 7 for the E_{corr} and Fig. 8

for the i_{corr} . Fig. 7b shows that E_{corr} decreased with an increase in the concentration of $(\text{NaPO}_3)_6$ almost linearly over the test range (0 ~ 200 ppm). Table 6 also confirms

that (NaPO₃)₆ is the most influential factor to E_{corr} among the additives in that the P-value is small as 0.008 and the coefficient is -0.0292. It means that 1 ppm of (NaPO₃)₆ causes decrease of E_{corr} by 0.0292 V according to the

Table 7. Regression results for i_{corr} (A/cm²) excluding outliers shown in Table 4 and Table 5

Term	Coefficient	P-value
Constant	7.29 × 10 ⁻⁶	0.000
NaNO ₂	8.70 × 10 ⁻⁷	0.356
(NaPO ₃) ₆	-4.021 × 10 ⁻⁶	0.000
TEA	1.319 × 10 ⁻⁶	0.173
Sugar	-1.992 × 10 ⁻⁶	0.038
Urea	1.218 × 10 ⁻⁶	0.207
NaNO ₂ *NaNO ₂	2.86 × 10 ⁻⁶	0.363
(NaPO ₃) ₆ *(NaPO ₃) ₆	4.25 × 10 ⁻⁶	0.182
TEA*TEA	1.04 × 10 ⁻⁶	0.739
sugar*sugar	-3.90 × 10 ⁻⁶	0.332
urea*urea	-9.2 × 10 ⁻⁷	0.770
NaNO ₂ *(NaPO ₃) ₆	-5.92 × 10 ⁻⁷	0.550
NaNO ₂ *TEA	1.049 × 10 ⁻⁶	0.285
NaNO ₂ *sugar	1.270 × 10 ⁻⁶	0.181
NaNO ₂ *urea	1.186	0.229
(NaPO ₃) ₆ *TEA	0.425	0.662
(NaPO ₃) ₆ *sugar	0.500	0.593
(NaPO ₃) ₆ *urea	-1.693	0.090
TEA*sugar	-2.441	0.015
TEA*urea	-1.236	0.203
sugar*urea	1.216	0.204

prediction of the regression model. The E_{corr} vs. NaNO₂, TEA, or urea plot showed an increase at low concentrations and a decrease at high concentrations. This implies that these compounds have a contradictory effect on E_{corr} in accordance with their concentration in the solution. Sugar appears to have a little effect on E_{corr}. However, we cannot be highly confident that NaNO₂, TEA, sugar, and urea behave as shown in the plots of Fig. 7 because their P-value are large (Table 6).

The corrosion potential is not a direct measure of corrosion resistance, because the corrosion potential is dependent on a complicated mechanism of anodic and cathodic reactions. The high corrosion potential possibly means good passivation by inhibitors, but it also proposes high susceptibility of pitting corrosion, due to the proximity to the pitting potential, in the CaCl₂ solution. In this work, the passivation properties and the pitting potential of steel in the various samples are not consistent and hence the comparative investigation on the corrosion potential in the point of corrosion resistance is not reasonable. The corrosion potential can be just a referable data but the corrosion rate at the corrosion potential is on the focus.

The i_{corr} was also affected by (NaPO₃)₆ most strongly (Fig. 8b). Figs. 8a and 8d show that NaNO₂ reduces i_{corr} only when its concentration is low and sugar reduces i_{corr} when its concentration is high. TEA and urea seem to increase i_{corr} slightly (Figs. 8c and 8e). Considering the P-values listed in Table 7, these plots are highly reliable for the effects of (NaPO₃)₆ and sugar but not for the others.

The effects of each factor can be modified by another factor. Such behaviors are perceived from the interaction

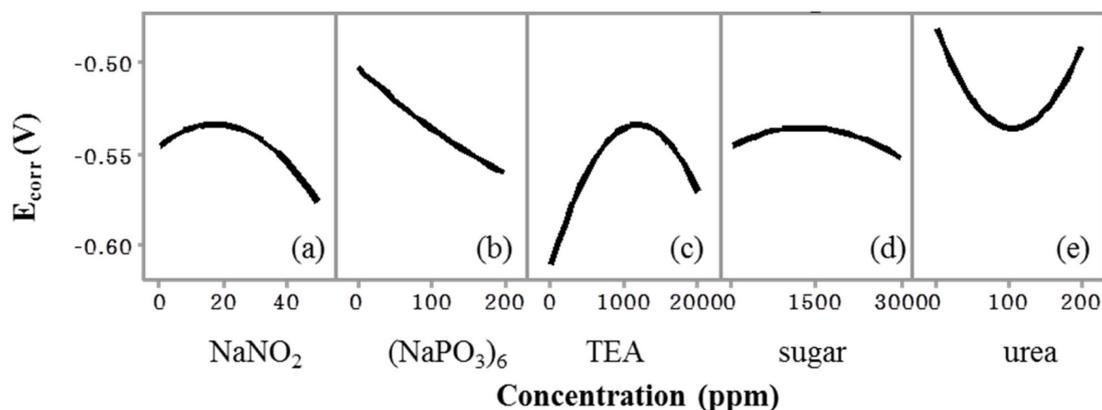


Fig. 7. Main effect plot of (a) NaNO₂, (b) (NaPO₃)₆, (c) TEA, (d) sugar, and (e) urea on E_{corr} of SPCC/S/B steel in the CaCl₂ solutions with the compositions as listed in Table 1

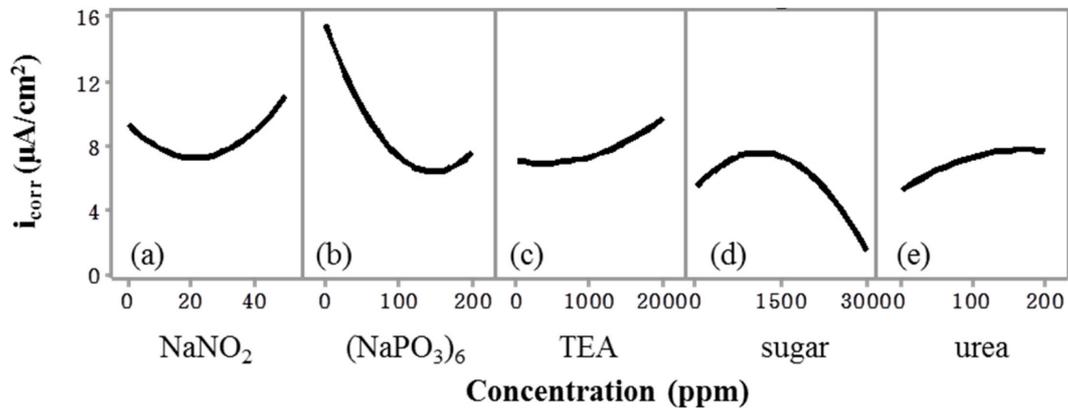


Fig. 8. Main effect plot (a) NaNO_2 , (b) $(\text{NaPO}_3)_6$, (c) TEA, (d) sugar, and (e) urea on i_{corr} of SPCC/S/B steel in the CaCl_2 solutions with the compositions as listed in Table 1

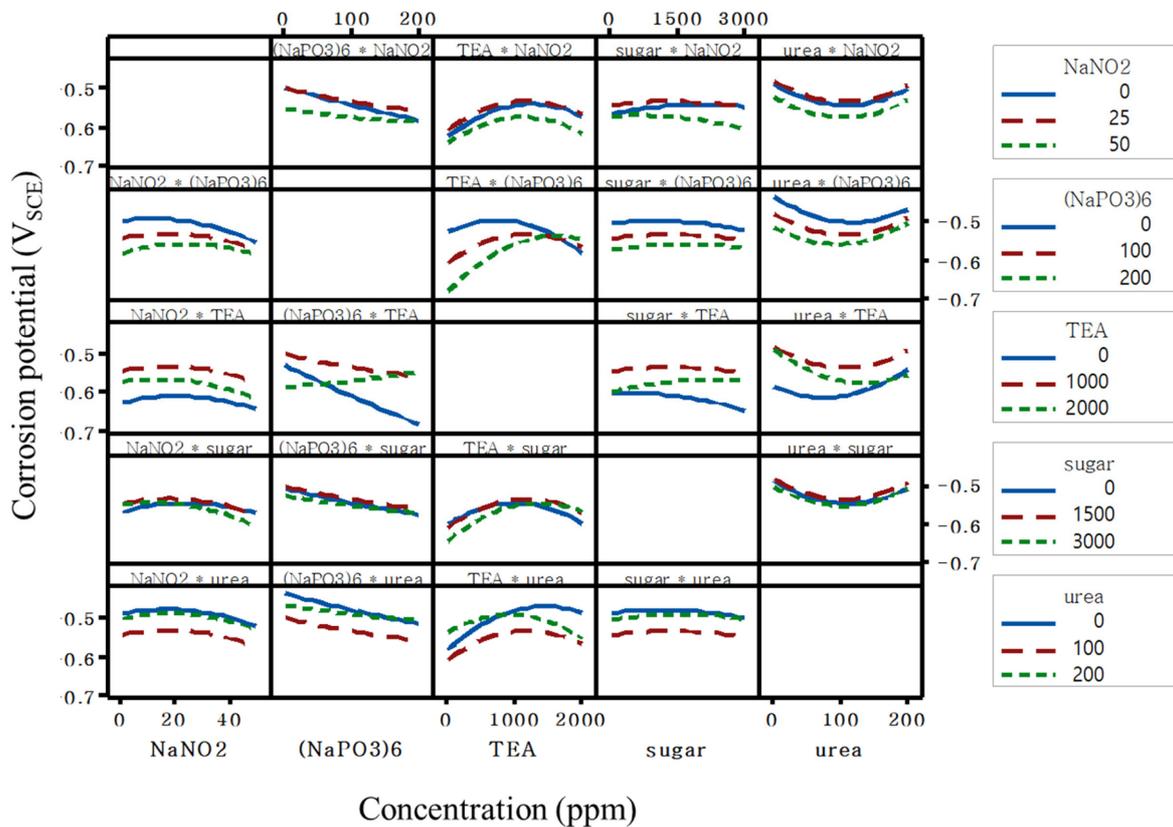


Fig. 9. Interaction plots for E_{corr} of SPCC/S/B steel in the CaCl_2 solutions with the compositions as listed in Table 1

plots as presented in Fig. 9. Fig. 9 are E_{corr} vs. concentration plots, in which each graphs have three curves corresponding to high, middle, and low concentration of another additive. The interaction plots of NaNO_2 (the first column in Fig. 9) indicate that the NaNO_2 slightly decreases the corrosion potential (E_{corr}) in general. The slope of the three curves in the NaNO_2 *urea plot, which are drawn with different

concentrations of urea, are almost constant although the values of E_{corr} are different with each other. It means that the effect of NaNO_2 on the E_{corr} is not changed by the concentration of urea. On the other hand, a change of slope in the NaNO_2 * $(\text{NaPO}_3)_6$ plots are noted. E_{corr} was decreased with an increase in the NaNO_2 concentration in the solution without $(\text{NaPO}_3)_6$ but it depended little on

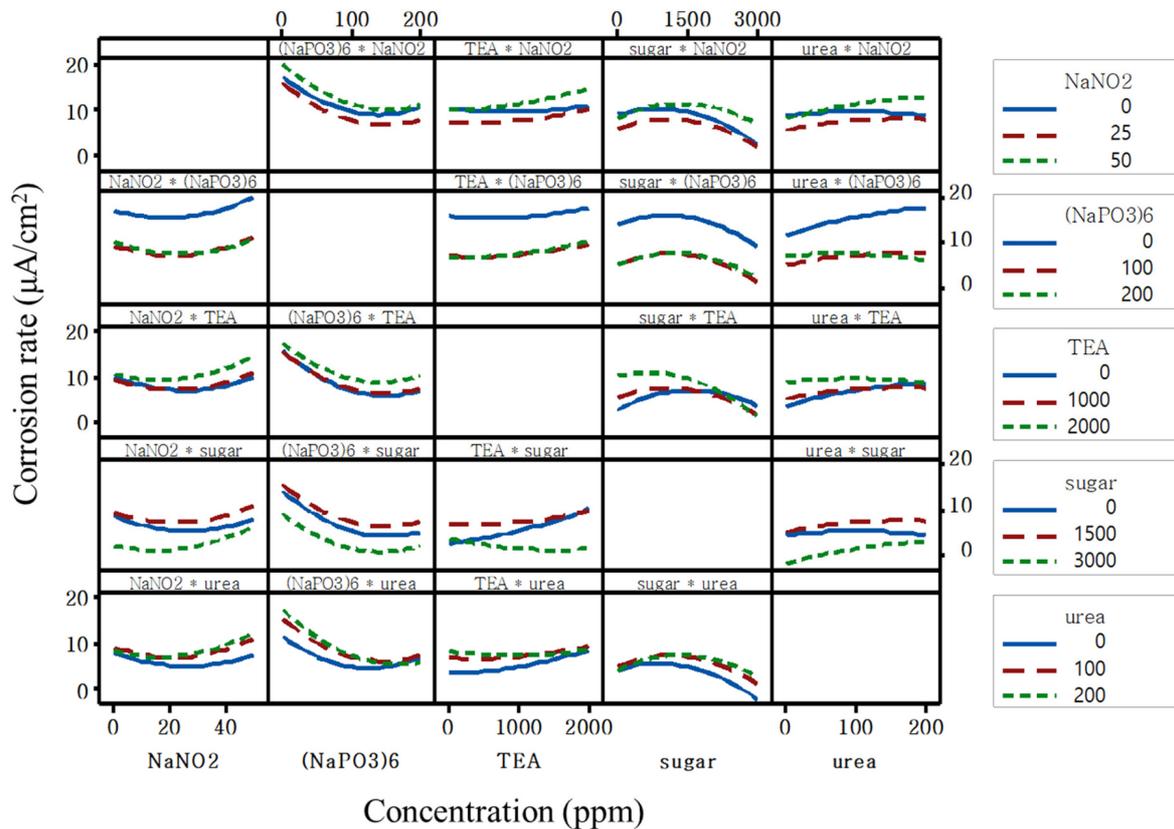


Fig. 10. Interaction plots for i_{corr} of SPCC/S/B steel in the CaCl₂ solutions with the compositions as listed in Table 1

the NaNO₂ concentration in the solution with 200 ppm (NaPO₃)₆. This implies that the NaNO₂ and (NaPO₃)₆ have an interaction. In this case, the effect of NaNO₂ is weakened by the addition of (NaPO₃)₆.

The interaction is the most significant for the (NaPO₃)₆ and TEA couple (the second and the third columns in Fig. 9). E_{corr} decreased remarkably with an increase of (NaPO₃)₆ concentration in the solution without TEA, however the slope of E_{corr} vs. (NaPO₃)₆ concentration plot was reversed by increasing the TEA concentration up to 2000 ppm. Similar behavior was also seen in the TEA*(NaPO₃)₆ plot. The main effect plot of (NaPO₃)₆ (Fig. 7) indicates only that (NaPO₃)₆ lowers E_{corr} but the interaction plot notes that the role of (NaPO₃)₆ is not the same when TEA is added together. TEA caused a gradual increase in E_{corr} with its concentration up to around 1000 ppm and then a decrease in most of TEA interaction plots except TEA*(NaPO₃)₆. The E_{corr} rose with an increase of TEA concentration up to about 3000 ppm in the solution with (NaPO₃)₆ at a high concentration as 200 ppm. Both (NaPO₃)₆ and TEA have small P-value from the regression

results (Table 7) and the concentration of these compounds will influence the E_{corr} predominantly. What should be noted from the interaction analysis (Fig. 9) is that the concentrations of (NaPO₃)₆ and TEA should be controlled together because the concentration of one of them will change the other's role.

The effect of sugar on E_{corr} was weak in general and interaction was rarely found (Fig. 9). Only TEA seems to interact with sugar a little, in that sugar decreased the E_{corr} in the solution without TEA but increased the E_{corr} slightly with 2000 ppm of TEA.

The interaction plots of urea also indicate that TEA interferes with urea while the other compounds do not (the last column in Fig. 9). Urea usually caused a slight decrease and then a slight increase of E_{corr} with increasing its concentration. Such behavior is corresponding to that with 1000 ppm TEA in the interaction plot of urea*TEA. However, the increasing effect of urea on E_{corr} was relatively strong in the solution without TEA, while the decreasing tendency was stronger with the higher TEA concentration.

Nevertheless, we should consider the P-value of the statistical analysis. Only the $(\text{NaPO}_3)_6$ *TEA ($P=0.000$), sugar*TEA ($P=0.079$), and urea*TEA ($P=0.013$) terms are important in a practical point of view.

Fig. 10 shows the interaction plots for i_{corr} . The TEA*sugar plot shows a clear interaction in which more than 1500 ppm of sugar is necessary to make TEA reduce the i_{corr} . Also, a high concentration of TEA enhances the effect of sugar reducing the i_{corr} as shown in the sugar*TEA plot. Urea appears to increase the slope of the curves slightly in the plots of NaNO_2 *urea, $(\text{NaPO}_3)_6$ *urea, TEA*urea, and sugar*urea. It means that urea weakens the effects of other compounds reducing the i_{corr} or make a neutral compound as TEA to increase the i_{corr} . Urea itself also increases the i_{corr} as shown in the main effect plot in Fig. 8. The interaction plots of urea (the last column of Fig. 10) indicates that this effect of urea is relatively prominent in the solution with a high content of NaNO_2 or sugar, implying a synergistic effect. But the addition of $(\text{NaPO}_3)_6$ or TEA suppresses an increase of i_{corr} by urea.

Consulting Table 7, only sugar*TEA couple has P-value lower than 0.05. The interaction terms including that for urea has P-values larger than 0.2, except $(\text{NaPO}_3)_6$ *urea which has $P = 0.090$. Therefore the interaction between the concentrations of sugar and TEA is highly recommended to be considered in designing the inhibitor composition to control i_{corr} . The interaction between $(\text{NaPO}_3)_6$ and urea can also be taken into account but its significance is not high.

The regression (Fig. 10) suggests that the corrosion rate is nearly minimized in the solution with the 3000 ppm of sugar, NaNO_2 less than 25 ppm, $(\text{NaPO}_3)_6$ more than 100 ppm, TEA more than 1000 ppm. It corresponds that the corrosion inhibition efficiency derived from the polarization tests (Table 3). The inhibition efficiency of no. 30, 43, and 44, which is following the above composition range, is higher than 68, 88, and 86%, respectively. It seems the inhibition efficiency is regardless of the concentration of urea of these samples, as explained by the high P-value in Table 7.

However, the minimum value from the regression is below zero and this is not realistic. In order to find the composition and the practically minimum corrosion rate, we need to design another experiment with the compositions at the vicinity of the possible optimum with a smaller

variation range. The reasonable corrosion rate can be predicted by regression when the experimental range is refined more.

The corrosion inhibiting effects evaluated in the laboratory may be extrapolated to the field environment for a long time as months or years, as long as the primary type of corrosion is the same and thus the inhibiting mechanism is valid. In the case of steel with the deicing agents, corrosion of steel will be progressed predominantly by general corrosion under wet-dry cycles. Although the tests in this study do not include wet-dry cycles, the inhibition rank to active dissolution was reasonably evaluated by polarization tests. We can consult it for the general corrosion situation. However, the prediction by potentiodynamic polarization tests will not be applicable when the thick rust or deposit layer accumulated on the steel surface and the influence of under-deposit corrosion or crevice corrosion becomes strong.

In summary of the statistical study, $(\text{NaPO}_3)_6$, TEA, and sugar are the major factor to E_{corr} . $(\text{NaPO}_3)_6$ lowers the E_{corr} and TEA make the E_{corr} higher. $(\text{NaPO}_3)_6$ and TEA have noticeable interaction. These two compounds also have an important role in controlling i_{corr} . $(\text{NaPO}_3)_6$ is the most effective inhibitor to reduce i_{corr} , having the largest negative coefficient (Table 7). TEA does not reduce the corrosion rate apparently, however it has interaction with sugar and makes sugar to reduce i_{corr} (Fig. 10).

It is reported from previous researches that hexameta-phosphate acts as an anodic inhibitor increasing the corrosion potential and promoting passivation [4] and also as a cathodic inhibitor [10,11]. For a passive metal, high corrosion potential can involve passivation and results in high corrosion resistance. However, the pitting potential is very low and a stable passive region was not recognized in this study, as shown in Fig. 1, due to the high concentration of chloride. Lowering corrosion potential should be the better way to reduce the corrosion rate in this case. Therefore $(\text{NaPO}_3)_6$ takes the most important role in inhibiting corrosion by lowering corrosion potential and the corrosion rate at the same time. Concerning the cathodic inhibiting, we could not find evidence in this study. The slope of the cathodic Tafel region was analyzed with RSM but no reasonable model was found.

TEA is known as an adsorption type inhibitor that reduces the activity of Cl^- by mainly chemisorption in the

active region and by hydrogen bond in the passive region [5,10]. It is also reported that TEA lowered the hydrogen evolution rate, corrosion potential, and corrosion rate of X-65 steel effectively up to its concentration of 250 ppm in 1 M HCl solution [12]. Similarly, the compounds of sugar, which are glucose, fructose, and galactose, easily adsorb on the metal surface and inhibit the adsorption of aggressive ions such as Cl⁻ [13-16]. Urea is also used extensively to suppress corrosion as an adsorption type inhibitor [5]. The effectiveness of organic inhibitors is known to depend on the molecular weight, as well as the electronic and chemical properties of the compound. The components of sugar, i.e., glucose, fructose, and galactose, have the molecular weight of 180.16 g/mol and the heaviest among the organic compounds used in this study. The molecular weight of TEA is 101.19 g/mol and that of urea is 60.06 g/mol. The significant effect of sugar reducing corrosion rate is thought to be related to the high molecular weight.

NaNO₂ is an anodic inhibitor [5] facilitating passivation, and effectively reduces corrosion rate [17-19]. Further, it may reduce the oxygen concentration in the solution by the reaction of $2\text{NaNO}_2 + \text{O}_2 \rightarrow 2\text{NaNO}_3$. However, we could not confirm the benefits of NaNO₂ in this study. The corrosion rate nor the cathodic current density show any clear trend with NaNO₂ concentration. It may be due to that the concentration of NaNO₂ is not sufficient to be required for passivation in the solution, considering that more than hundreds of ppm of NaNO₂ was used to obtain a significant inhibiting effect in previous studies [20,21].

5. Conclusions

The corrosion behavior of carbon steel in the 3 wt% CaCl₂ solutions containing 0 ~ 50 ppm sodium nitrite, 0 ~ 200 ppm sodium hexametaphosphate, 0 ~ 2000 ppm trimethylamine, 0 ~ 3000 ppm sugar, and 0 ~ 100 ppm urea was examined by potentiodynamic polarization tests. The corrosion potential and corrosion rate were statistically analyzed by Response Surface Methodology (RSM). The findings from the study are as follows:

- 1) Hexametaphosphate, trimethylamine, and sugar inhibit corrosion effectively in CaCl₂ solution.
- 2) Hexametaphosphate significantly reduced the corrosion rate and lowered the corrosion potential.

- 3) Trimethylamine itself was not effective in reducing the corrosion rate but it enhanced the inhibiting effect of sugar.
- 4) The significant effects of sugar is thought to be related to its high molecular weight, while the effects of urea is not noticeable because the molecular weight of urea is low.
- 5) The effects of sodium nitrite was negligible in this study presumably due to the insufficient concentration in the solution.

Acknowledgments

This study was supported by research fund from Chosun University, 2019. We also acknowledge Korea Agency of Environment (KENA), Inc. for supplying the test materials.

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