

Article

Investigating the Synergistic Corrosion Protection Effect of an Alloy Element and Corrosion Inhibitor on Steel Reinforcement Using Machine Learning and Electrochemical Impedance Spectroscopy

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Abstract: Steel reinforcement in marine concrete structures is vulnerable to chloride-induced corrosion, which compromises its structural integrity and durability. This study explores the combined effect of the alloying element Cr and the smart corrosion inhibitor LDH-NO₂ on enhancing the corrosion resistance of steel reinforcement. Employing a machine learning approach with a support vector machine (SVM) algorithm, a predictive model was developed to estimate the polarization resistance of steel, considering Cr content, LDH-NO₂ dosage, environmental pH, and chloride concentration. The model was rigorously trained and validated, demonstrating high accuracy, with a correlation coefficient exceeding 0.85. The findings reveal that the addition of Cr and application of LDH-NO₂ synergistically improve corrosion resistance, with the model providing actionable insights for selecting effective corrosion protection methods in diverse concrete environments.

Keywords: machine learning; steel reinforcement; corrosion; LDH-NO₂; Cr



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1. Introduction

In marine concrete structures, the corrosion of steel reinforcement presents a significant challenge, posing threats to the durability and safety of infrastructure worldwide [1]. The corrosive agents in seawater, especially chloride ions, accelerate the degradation process, leading to substantial maintenance costs and structural integrity concerns. This issue is of particular concern in coastal and marine environments, where concrete structures are frequently exposed to harsh conditions. To combat these challenges, various corrosion protection techniques have been developed and employed in marine engineering, including alloy steel reinforcement [2], coatings [3], cathodic protection [4], and corrosion inhibitors [5].

Among the various techniques, the incorporation of the alloying element chromium (Cr) into steel has emerged as a crucial strategy to enhance corrosion resistance. There has been a significant amount of research on the influence of Cr in enhancing the corrosion resistance of steel reinforcement, and there are even corrosion-resistant steel reinforcements with different Cr contents available for purchase [6–10]. The improved corrosion resistance provided by Cr is multifactorial. On the one hand, Cr forms a passive oxide layer on the surface of the steel, acting as a barrier against corrosive agents, thereby extending the chloride-induced de-passivation time of the reinforcement [8]. On the other hand, Cr infiltrates the rust layer on the steel surface, altering its morphology, composition, and structure, thus prolonging the time before concrete cracking occurs [11,12]. As a result, the incorporation of Cr as an alloying element can augment the corrosion resistance of steel reinforcement in harsh environments, thereby prolonging the service life of concrete

structures and improving their safety. Therefore, it is evident that Cr-containing steel reinforcement offers considerable potential for utilization in marine engineering projects.

However, it has been observed in engineering applications that a significant issue arises when using Cr-containing steel reinforcement in chloride-contaminated concrete: Cr, as an alloying element, can markedly increase the susceptibility of the reinforcement to pitting corrosion. In other words, while the average corrosion rate of Cr-containing steel reinforcement may not be high in marine environments, severe corrosion and thinning of the steel cross-section can occur in localized areas. To address this problem, the use of smart corrosion inhibitors is considered to be a promising approach to mitigate the shortcomings of Cr-containing steel reinforcement [13]. Smart corrosion inhibitors are designed to store corrosion inhibitors in low-corrosion-risk areas, while rapidly releasing the inhibitors in high-corrosion-risk areas. The synergistic use of Cr-containing steel reinforcement and smart corrosion inhibitors not only maintains the excellent corrosion resistance of Cr-containing steel reinforcement but also further suppresses its localized corrosion.

The “LDH-inhibitor” system is currently one of the research hotspots within the field of smart corrosion inhibitors [14]. In this system, LDH refers to layered double hydroxides (chemical formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$, where M^{2+} and M^{3+} represent metal cations, and x is the percentage of M^{3+}), and the “inhibitor” component comprises negatively charged corrosion inhibitor ions (such as nitrite (NO_2^-) and phosphate (PO_4^{3-})). The positively charged LDH layers and the negatively charged inhibitor ions are held together through electrostatic interactions. In the presence of anions in the surrounding environment exerting a stronger electrostatic effect on the LDH layers, the LDH will adsorb these environmental anions and simultaneously release the corrosion inhibitor ions through ion-exchange reactions. In other words, in areas with a high risk of corrosion, where chloride ions are present, the LDH-inhibitor can rapidly release inhibitor ions through ion-exchange reactions (LDH-inhibitor + chloride ions = LDH-chloride + inhibitor ions). Consequently, the LDH in the LDH-inhibitor system functions as an intelligent carrier for inhibitor ions, ensuring that the latter are stored in low-corrosion-risk areas devoid of chloride and released in high-corrosion-risk areas containing chloride. Therefore, the LDH-inhibitor smart corrosion inhibitor can guarantee the exceptional corrosion resistance of Cr-containing steel reinforcement while specifically targeting and mitigating pitting corrosion.

However, existing studies predominantly focus on the impact of individual protective technologies on steel corrosion in concrete. Each technique has its own advantages and limitations, and combining two or more methods can enhance their effectiveness through mutual reinforcement, achieving a cumulative effect greater than the sum of the individual measures. Furthermore, practical engineering applications often require the synergistic use of multiple protective techniques. Therefore, this study investigates the synergistic corrosion protection effect of Cr and LDH- NO_2 (in which the inhibitor ions are NO_2^-) on steel reinforcement. It aims to significantly reduce the average corrosion rate of steel reinforcement through the use of the alloying element Cr, while employing the smart inhibitor LDH- NO_2 to specifically target and repair localized corrosion damage in Cr-containing steel, ultimately ensuring effective corrosion protection over the entire service life of the reinforcement.

In the conventional experimental approach to investigating multi-factor interactions, techniques such as orthogonal experiments and factor analysis are frequently employed. However, these methods have inherent limitations in their ability to handle high-dimensional, multi-variable complex interactions, and they can also be quite cumbersome in terms of experimental design and data analysis. In contrast, advanced machine learning methods offer significant advantages, particularly in terms of automating data processing and model training. Such techniques can identify intricate non-linear relationships and multi-factor interactions that may otherwise remain obscured within the data, thereby facilitating more precise predictions.

Specifically, the aim of this study is to assess the corrosion resistance of steel reinforcement in concrete under different levels of chloride ion contamination and carbonation,

considering the content of the alloy element Cr and the dosage of the smart corrosion inhibitor LDH-NO₂. The vast range of environmental factors in concrete and the flexibility in adjusting steel's Cr content and concrete's LDH-NO₂ dosage pose significant challenges for the comprehensive quantification of their relationships. Moreover, due to the complex, non-linear relationship between the corrosion rate and multiple variables, traditional single-variable fitting methods are inadequate. Therefore, advanced machine learning techniques are primarily employed in this research to accurately model these intricate relationships and examine the impact of steel reinforcement Cr content, LDH-NO₂ dosage, concrete chloride concentration, and pore solution pH on corrosion resistance. Correlation models between these factors and steel reinforcement polarization resistance are developed to guide the selection of corrosion prevention methods for concrete structures with varying degrees of corrosion risk.

2. Methods

2.1. Establishment of Quantitative Predictive Model

First, a large number of data samples on the influence of steel's Cr content and corrosion inhibitor LDH-NO₂ dosage on the polarization resistance of steel reinforcement were collected from the literature. Then, advanced machine learning techniques were employed to achieve accurate fitting of complex non-linear relationships and explore the influence of Cr content and LDH-NO₂ dosage, environmental chloride concentration, and pH value on the corrosion resistance of steel reinforcement. A correlation model between these factors and the polarization resistance of steel reinforcement was obtained to achieve rapid prediction. Through the preliminary evaluation of commonly used machine learning regression algorithms such as linear regression, neural networks, random forest, support vector machine (linear kernel), support vector machine (Gaussian kernel), and K-nearest neighbors, the final selection for the machine learning prediction model was based on the good performance observed on the data samples, leading to the choice of random forest and support vector machine (Gaussian kernel) models.

Specifically, in the process of evaluating the generalization performance of the machine learning models, 80% of the data samples were used as a training set to train and establish the machine learning model, and the model parameters were optimized by ten-fold cross validation. The other 20% of the data samples were used as a test set to assess the generalized predictive capability of the model. The Pearson correlation coefficient r^2 and the mean absolute error (MAE) were chosen based on the prediction results of the machine learning model for test set samples; as the main evaluation index, the expression for r^2 is as follows:

$$r^2 = \frac{\sum (X - \bar{X})(Y - \bar{Y})}{(\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2})(\sqrt{\sum_{i=1}^n (Y_i - \bar{Y})^2})}$$

where $\bar{X}$ and $\bar{Y}$ represent the means of variables X and Y , respectively, while X_i and Y_i represent the variable values corresponding to each sample, denoting the experimental and model-predicted values of the data sample i . From this, the value of r^2 is approximately closer to 1, indicating a better correlation between the model prediction result and the experimental value, implying a better generalization ability of the model. As for MAE, its expression is as follows:

$$\text{MAE} = \frac{\sum_{i=1}^n |y - y_i|}{n}$$

where n represents the number of samples, y_i represents the actual value of sample i , and y represents the corresponding model-predictive results. A lower MAE indicates a smaller deviation between the predicted results of the model and the experimental value, signifying a better generalization ability of the model. Furthermore, in order to eliminate the accidental influence of the 80–20% data partition on the model prediction results, we took 100 data partitions, averaging the results, in order to compare the predictive generalization performance of each machine learning model.

Using the collected training data, with the Cr content, LDH-NO₂ dosage, chloride concentration, and pH value as the inputs of the model, and with the experimental value of polarization resistance of the steel reinforcement as the output of the model, we evaluated and selected the machine learning model, and the predictive model of polarization resistance of steel reinforcement was established. In addition, in order to eliminate the effect of the input data dimensions on the model fitting, in the process of evaluating the machine learning models, a 0–1 standardization was applied to the input variables (Cr content, LDH-NO₂ dosage, chloride concentration, and pH value) to eliminate the impact of dimensionality on distance-based machine learning models, such as the K-nearest neighbors model. At the same time, in order to avoid overfitting, the ten-fold cross-validation method was used to select certain machine learning models, executing prediction. Specifically, all data samples were divided into ten equal parts, with the model trained using nine parts and the remaining one part used for prediction. The prediction results of each sample were obtained successively. Each sample was not utilized in the model training process, ensuring the reliability of the model predictions. Furthermore, in order to analyze and ensure the stability of the machine learning models' prediction, 100 cross-validations were performed to validate the model predictions.

2.2. Validation of Quantitative Prediction Model

Steel reinforcements with varying Cr contents were prepared using vacuum melting and rolling processes. The chemical composition is detailed in Table 1.

Table 1. Chemical composition of the steel reinforcement.

Label of Steel	C Content (wt%)	Mn Content (wt%)	Si Content (wt%)	S Content (wt%)	P Content (wt%)	Cr Content (wt%)
0 Cr	0.23	1.57	0.57	0.005	0.024	0.05
1 Cr	0.16	0.58	0.26	0.005	0.004	1.02
2 Cr	0.10	0.69	0.47	0.005	0.003	2.46
5 Cr	0.04	1.07	0.56	0.006	0.003	5.21

The smart corrosion inhibitor LDH-NO₂ was also prepared using the hydrothermal reaction method. A 50 mL mixture of 0.5 mol/L Zn(NO₃)₂ and 0.25 mol/L Al(NO₃)₃ was slowly added to a 100 mL solution of 1 mol/L NaNO₂ at a drip rate of 50 mL/h, with a temperature of 65 °C, maintaining the pH at 10 ± 0.3 using 1 mol/L NaOH solution and vigorous stirring. After titration, the suspension was crystallized in a high-pressure autoclave at 70 °C for 24 h, followed by filtration, washing, freeze-drying, and grinding [15].

Electrochemical impedance spectroscopy (EIS) was used to test the polarization resistance of steel reinforcements with varying Cr contents under different pH levels and chloride concentrations in simulated concrete solutions with different LDH-NO₂ dosages. The polarization resistance was fitted using ZSimpWin software (version 3.6). Specifically, a three-electrode system was used, with the steel samples employed as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The working electrodes were all pre-passivated in saturated calcium hydroxide for 7 days before EIS testing. The test solution comprised a chloride-carbonated concrete simulated pore solution, with the pH adjusted using sodium carbonate and sodium bicarbonate. The frequency range for electrochemical impedance spectroscopy testing was from 100 kHz to 10 mHz, with an amplitude of 10 mV.

Finally, the prediction model in Section 2.1 was validated using the measured polarization resistance values from Section 2.2.

3. Results and Discussion

3.1. Preliminary Machine Learning

Table A1 [15–22] presents a total of 106 data samples collected from the literature, encompassing information on steel rebar Cr content, LDH-NO₂ dosage, concrete chloride concentration, and pore solution pH value. In the process of machine learning, the input variables include the Cr content, the LDH-NO₂ dosage, chloride concentration, and pH value. The target variable (output variable) is the polarization resistance of the steel reinforcement. Using the above data, the generalized predictive ability of seven commonly used algorithm models was evaluated, including the linear regression model (LM), linear kernel support vector machine model (SVR.lin), artificial neural network model (NN), Gaussian regression model (GPR), K-nearest neighbors model (KNN), Gaussian kernel support vector machine model (SVR.rbf), and random forest model (RF). The correlation and error of each prediction model are illustrated in Figure 1a, with the performance evaluation metrics, including r^2 and MAE, representing the average of 100 predictions. The volatility of each model is indicated by error bars. From Figure 1a, it is evident that the SVR.rbf model exhibits the poorest prediction performance, with a correlation coefficient below 0.5 between the predicted and experimental values, and relatively large prediction errors, as indicated by the wide error bars, highlighting its instability in predictions. The predictive performance of the LM, SVR.lin, NN, GPR, and KNN models shows no significant differences, with correlations consistently around 0.6. Among these, the artificial neural network model (NN) exhibits slightly less effectiveness. The random forest (RF) model demonstrates the highest performance among all models, achieving a predicted correlation coefficient of 0.65, with an average prediction error of 334 kΩ·cm² for polarization resistance. Consequently, the RF model was chosen as the preferred predictive model, and its cross-validation results are depicted in Figure 1b. It can be observed that the model predictions vary significantly across the entire numerical range of polarization resistance, particularly in the low- and high-value ranges, resulting in an overall less-than-satisfactory prediction performance.

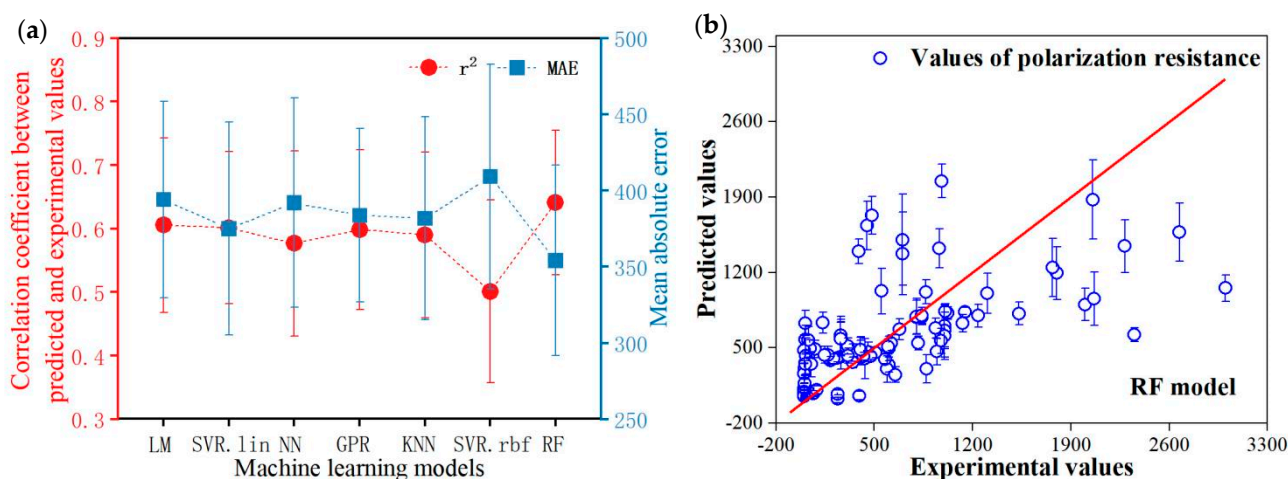


Figure 1. (a) Comparison of prediction performance of different machine learning models. (b) Prediction results of the random forest model (RF) for polarization resistance.

In-depth analysis of the results from each machine learning model revealed that the differences in their generalization performance are not pronounced. Particularly notable is the Gaussian kernel support vector machine model (SVR, rbf), which is typically esteemed for its performance with small data samples but exhibited the weakest performance in this context. Moreover, the presence of larger error bars suggests potential overfitting in the model predictions. The poor model performance can be attributed to the significant influence of experimental conditions, such as the composition of steel reinforcement, in-

interface status, pre-passivation time, and the test system, on the corrosion resistance of the steel reinforcement. Additionally, variations in the testing conditions for the polarization resistance of steel reinforcement samples were not accounted for in the model fitting process, resulting in negligible differences in model performance. The robust SVR.rbf model, renowned for its fitting capability, paradoxically demonstrates inferior performance. Therefore, to investigate the influence of Cr content and LDH-NO₂ dosage on the polarization resistance of steel reinforcement, it is imperative to re-clean and refine the training data.

3.2. Machine Learning after Data Cleaning

Due to the significant variance in corrosion mechanisms between high-alloy and low-alloy steel, the Cr content range was specified as 0–5 wt%. Considering actual concrete conditions, the LDH-NO₂ and chloride concentrations were defined within the ranges of 0–0.5 wt% and 0–3.5 wt%, respectively, while the pH value ranged from 9.5 to 12.5. Additionally, due to the significant impact of specific experimental procedures on the surface condition and corrosion rates of the steel reinforcement, only the corrosion data from pre-passivated steel reinforcement were selected. After the aforementioned data cleaning process, a total of 52 data samples remained, as detailed in Table A2.

Figure 2a demonstrates the predictive performance of each trained machine learning mode using the cleaned data. A comparison with Figure 1a reveals a notable enhancement in simulation prediction accuracy, stemming from the elimination of test condition influences on the polarization resistance of the steel reinforcement. In Figure 2a, the LM and SVR.lin models demonstrate similar generalization abilities, whereas the random forest (RF) model exhibits the lowest predictive correlation and higher prediction error. The prediction error of the KNN model is comparable to that of the SVR.rbf model, but the SVR.rbf model shows higher correlation in its prediction results. After careful consideration, the SVR.rbf model was chosen as the final predictive model. Figure 2b illustrates the correlation between the polarization resistance predicted by the Gaussian kernel support vector machine model (SVR.rbf) and the experimental data. Despite notable deviations for two samples in the low-value range, the model demonstrates overall excellent predictive performance. The correlation coefficient between the predicted and experimental values exceeds 0.85. For polarization resistances greater than 100 kΩcm², the root-mean-square error is only 5.2 kΩcm². Furthermore, the prediction error bar, derived from 100 cross-validations, is relatively narrow, indicating the robust predictive stability of the selected support vector machine model.

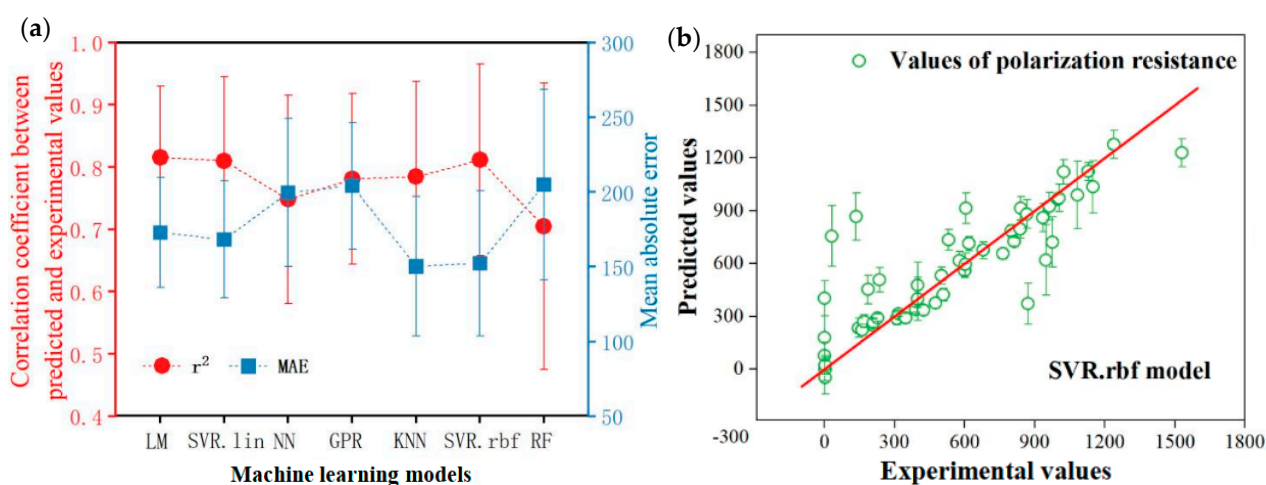


Figure 2. (a) Comparison of prediction performance of different machine learning models. (b) Prediction results of the Gaussian kernel support vector machine model (SVR.rbf).

3.3. Establishment of Prediction Model

Using the predictive capabilities of the Gaussian kernel support vector machine model (SVR.rbf), the distribution of polarization resistance in the steel reinforcement was obtained under varying Cr contents (0–5 wt%), LDH-NO₂ dosages (0–0.5 wt%), concrete chloride concentrations (0–3.5 wt%), and pore solution pH values (9.5–12.5). The original data for this predictive model were derived from electrochemical measurements taken during the direct immersion of steel reinforcement samples in simulated pore solutions. Consequently, this model is only applicable to conditions where the pore solution of the concrete or mortar is water-saturated.

Figure 3 depicts the evolution of the polarization resistance of steel reinforcement with environmental pH value and chloride concentration at a specific steel Cr content and LDH-NO₂ dosage. It is evident that, in the experimental system without the addition of the alloying element Cr and the smart inhibitor LDH-NO₂, the polarization resistance of the steel reinforcement exhibits a gradual decrease with a decrease in pH and an increase in chloride concentration. At a relatively high pH of 12.5, a notable decline in the polarization resistance of the steel reinforcement is only discernible at exceedingly elevated chloride concentrations. Conversely, at a relatively low pH of 10, a notable reduction in polarization resistance is observed at lower chloride concentrations. These findings are in accordance with the empirical observations.

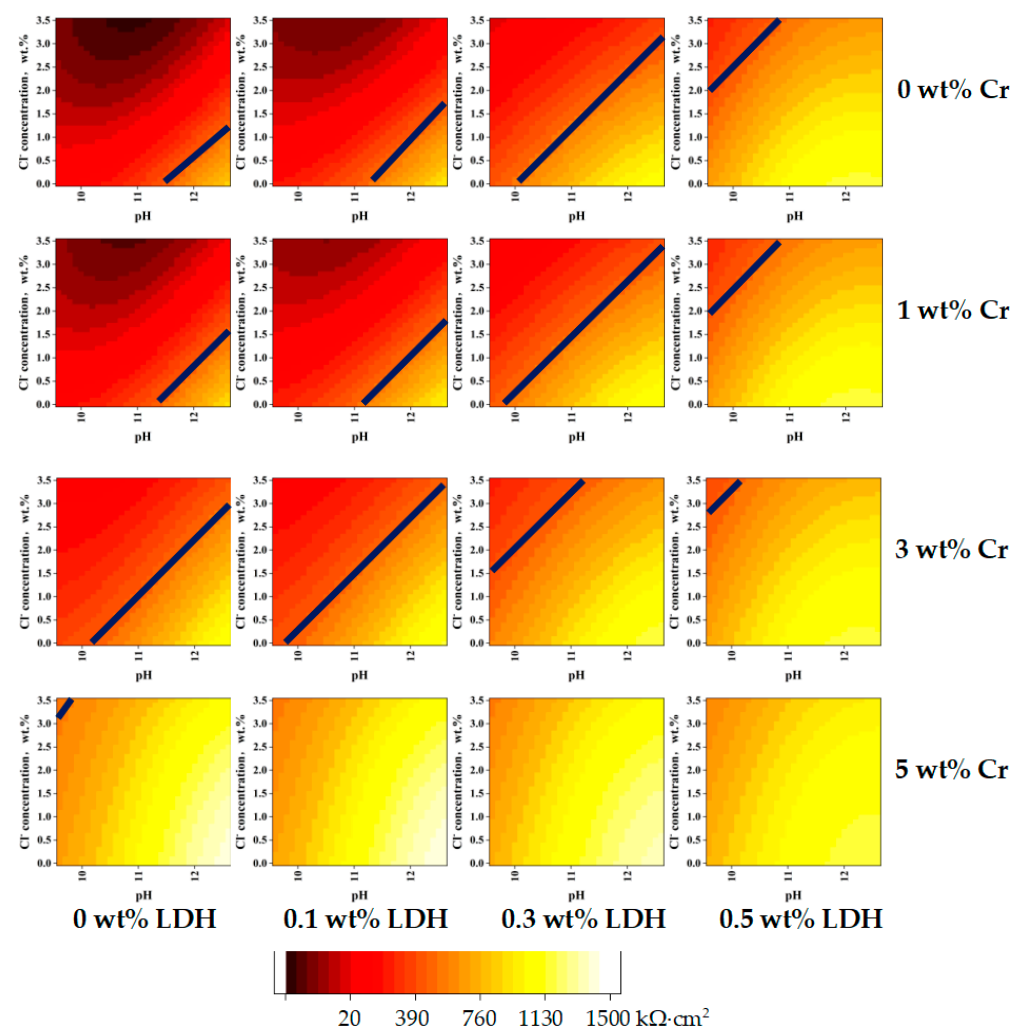


Figure 3. Influence of concrete pH value and chloride concentration on polarization resistance under specific steel reinforcement Cr contents and corrosion inhibitor LDH-NO₂ dosages.

Generally, in steel-reinforced concrete systems, corrosion is considered to be negligible when the corrosion rate is less than $0.1 \mu\text{A}\cdot\text{cm}^{-2}$ and the corresponding polarization resistance is $520 \text{ k}\Omega\cdot\text{cm}^2$ [23]. Therefore, polarization resistances greater than $520 \text{ k}\Omega\cdot\text{cm}^2$ can be used as an indicator that corrosion has not yet occurred. For carbon steel reinforcement with a Cr content of 0, the polarization resistance starts below $520 \text{ k}\Omega\cdot\text{cm}^2$ when the environmental pH is below 12 and the chloride concentration exceeds 0.5 wt%. This indicates that carbon steel can only maintain a passive state in concrete with a pH greater than 12 and a chloride concentration less than 0.5 wt%. Therefore, using plain carbon steel reinforcement in marine concrete engineering presents a high corrosion risk.

It is evident that independently increasing the Cr content in the steel reinforcement or the LDH-NO₂ dosage in the concrete can enhance the polarization resistance of the steel reinforcement under identical environmental conditions. When the Cr content in steel increases to 1 wt%, the increase in polarization resistance is not significant, indicating a slight improvement in corrosion resistance compared to carbon steel. However, at a Cr content of 3 wt%, the polarization resistance begins to drop below $520 \text{ k}\Omega\cdot\text{cm}^2$ in the concrete environment with pH 11.5 and 1 wt% chloride, showing a notable improvement compared to carbon steel. At 5 wt% Cr content, the polarization resistance generally exceeds $520 \text{ k}\Omega\cdot\text{cm}^2$ within the pH range of 12.5 to 9.5 and chloride concentrations ranging from 0 to 3.5 wt%, indicating excellent corrosion resistance. Using the corrosion inhibitor LDH-NO₂ can also effectively reduce the corrosion rate of steel reinforcement. With an increase in LDH-NO₂ dosage, the polarization resistance of the steel improves relatively linearly. When the LDH-NO₂ dosage is 0.1 wt%, the polarization resistance of the steel reinforcement begins to drop below $520 \text{ k}\Omega\cdot\text{cm}^2$ in an environment with pH 12 and 0.7 wt% chloride. As the LDH-NO₂ dosage reaches 0.5 wt%, the polarization resistance starts to decrease below $520 \text{ k}\Omega\cdot\text{cm}^2$ in an environment with pH 10.5 and 2.5 wt% chloride. Moreover, adding 0.2 wt% LDH-NO₂ to the concrete has a similar effect to adding 3 wt% Cr to the steel, while adding 0.5 wt% LDH-NO₂ has a similar effect to adding 4 wt% Cr.

The combined use of Cr and LDH-NO₂ demonstrates greater effectiveness compared to using either alloy elements or corrosion inhibitors alone. In Figure 3, the blue line represents a scenario where the polarization resistance of the steel reinforcement measures $520 \text{ k}\Omega\cdot\text{cm}^2$. The upper left corner of the blue line indicates corroded steel reinforcement, while the lower right corner signifies non-corroded steel reinforcement. It is evident that the simultaneous application of the alloy element Cr and the corrosion inhibitor LDH-NO₂ expands the area in the lower right corner where the steel reinforcement remains non-corroded. When adding only the alloy element Cr, 5 wt% Cr is required to significantly expand the range of pH and chloride concentrations where the steel reinforcement remains non-corroded. When using only the corrosion inhibitor LDH-NO₂, 0.5 wt% LDH-NO₂ is needed to achieve the same effect. However, when 3 wt% Cr and 0.3 wt% LDH-NO₂ are used synergistically, the range of pH and chloride concentrations where the steel reinforcement remains non-corroded can be significantly expanded.

Figure 4 describes the required Cr content of the steel and LDH-NO₂ dosage to maintain the polarization resistance of steel above $520 \text{ k}\Omega\cdot\text{cm}^2$ at specific concrete pH values and chloride concentrations. In concrete severely affected by carbonation and chloride intrusion (pH 10 + 3.5 wt% Cl[−]), to ensure adequate passivation of the steel reinforcement (polarization resistance $> 520 \text{ k}\Omega\cdot\text{cm}^2$), steel with 5 wt% Cr is required, or alternatively, 3 wt% Cr modified steel combined with 0.4 wt% LDH-NO₂. In environments where carbonation is less severe but chloride intrusion is significant (pH 12 + 3.5 wt% Cl[−]), steel with 3 wt% Cr is necessary for ensuring steel's passivation, or alternatively, steel modified with 1 wt% Cr combined with 0.4 wt% LDH-NO₂ can be considered.

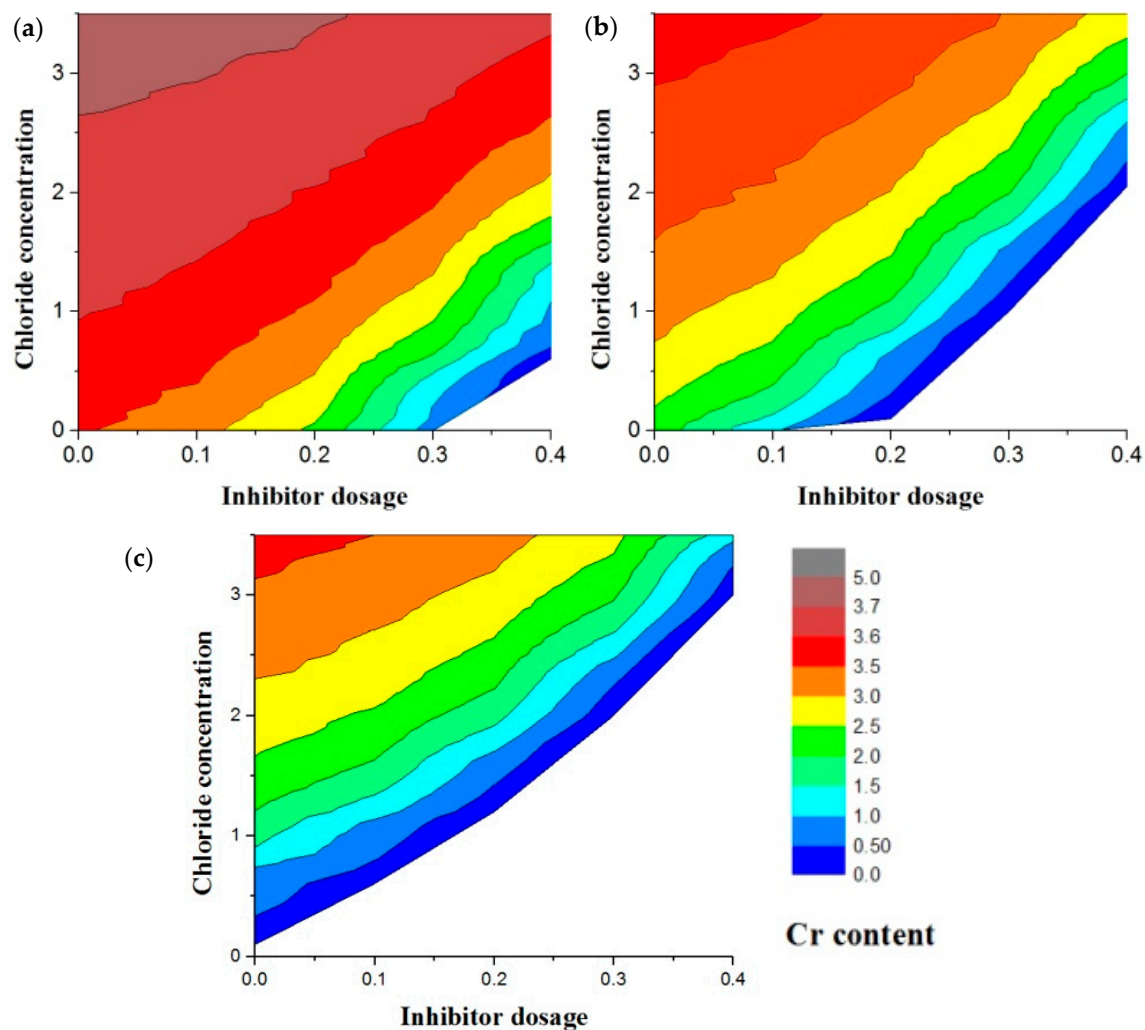


Figure 4. At a specified level of concrete carbonation, the necessary Cr content of the steel reinforcement and the dosage of the corrosion inhibitor LDH-NO₂ required to ensure a polarization resistance exceeding 520 kΩ·cm²: (a) pH 10, (b) pH 11, (c) pH 12.

3.4. Validation of the Prediction Model

To verify the polarization resistance models obtained from Figure 3, a batch of Cr-modified steel bars and the smart corrosion inhibitor LDH-NO₂ were prepared in this study. Figure 5 shows the EIS of steel bars in the simulated concrete pore solution with different Cr contents and LDH-NO₂ dosages. A fitting was conducted using the equivalent circuit shown in Figure 6, where R_s represents the solution resistance, R_{ct} stands for the charge-transfer resistance, R_f for film resistance, R_p for polarization resistance, Q_{dl} for double-layer capacitance, and Q_f for film capacitance. Due to the rough and uneven electrode interface, a constant-phase element (Q) is employed to replace capacitance, with an impedance of

$$Z_Q = \frac{1}{Q_0(j\omega)^n}$$

where ω is the angular frequency, j is the imaginary unit, and n is the exponent of the constant-phase element. Furthermore, the total impedance (Z) of the system is

$$Z = R_s + \frac{1}{Z_{Q_{dl}} + \frac{1}{R_{ct} + \frac{1}{Z_{Q_f} + R_f}}}$$

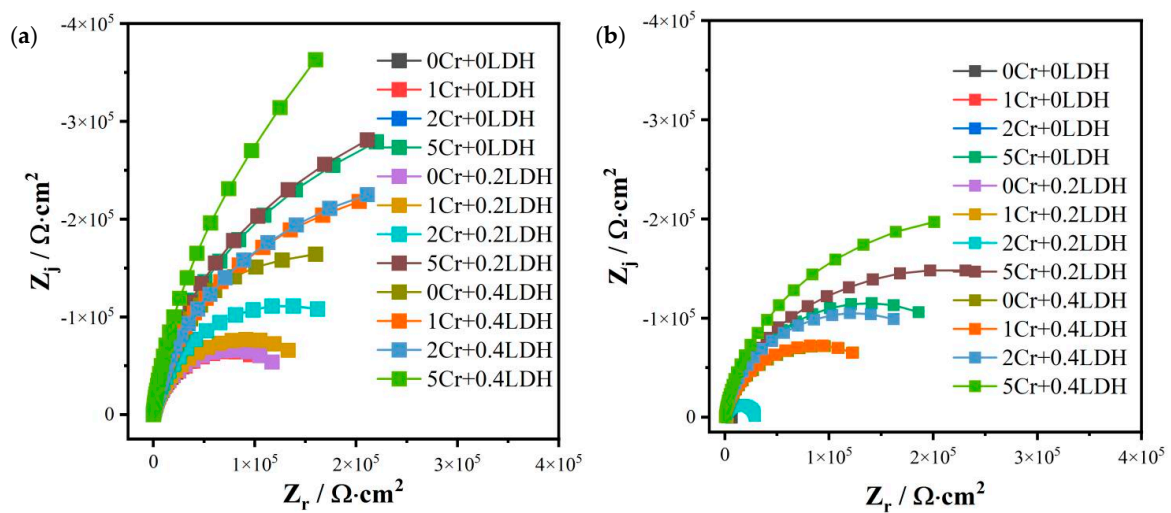


Figure 5. Electrochemical impedance spectra of steel bars in the simulated concrete pore solution with different Cr contents and LDH–NO₂ dosages: (a) pH 12 and 3.5 wt% chloride in the solution; (b) pH 10 and 3.5 wt% chloride in the solution.

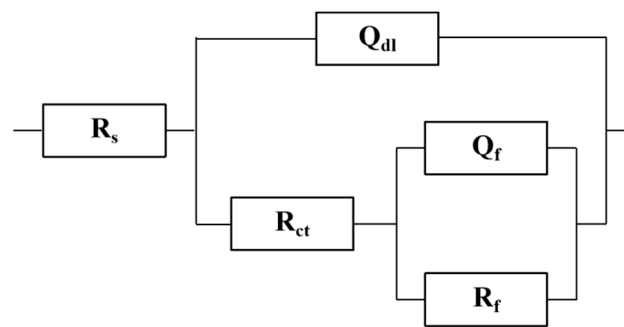


Figure 6. Equivalent circuit.

The fitting results of the EIS in Figure 5 are presented in Tables 2 and 3. Observably, as the Cr content or LDH–NO₂ dosage increases, the polarization resistance of the steel bar increases. The correlation between the measured polarization resistance (R_p) in Tables 2 and 3 and the predicted R_p from Figure 3 is depicted in Figure 7. It is evident that the measured R_p values closely correspond to the predicted ones, further confirming the efficacy of the predictive model.

Table 2. Parameters of electrochemical impedance spectra in Figure 5, where the pH of the solution was 12 and the chloride concentration was 3.5 wt%.

Cr Content	LDH–NO ₂ Dosage	Q_f ($\mu\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^n$)	n	R_f ($\text{k}\Omega\cdot\text{cm}^2$)	Q_{dl} ($\mu\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^n$)	n	R_{ct} ($\text{k}\Omega\cdot\text{cm}^2$)	$R_p = R_f + R_{ct}$ ($\text{k}\Omega\cdot\text{cm}^2$)
0 wt%	0 wt%	59	0.92	91	32	0.89	57	148
1 wt%	0 wt%	2	0.67	0.02	54	0.91	161	161
2 wt%	0 wt%	38	0.91	154	115	1	24	178
5 wt%	0 wt%	35	0.94	140	18	0.81	116	256
0 wt%	0.2 wt%	179	0.96	0.008	204	0.92	278	278
1 wt%	0.2 wt%	15	1	0.1	16	0.84	502	502
2 wt%	0.2 wt%	28	0.93	448	16	0.96	215	663
5 wt%	0.2 wt%	16	1	0.1	14	0.85	694	694
0 wt%	0.4 wt%	1	0.65	0.07	38	0.92	416	416
1 wt%	0.4 wt%	0.02	0.79	0.04	44	0.90	612	612
2 wt%	0.4 wt%	27	0.93	0.001	2	0.44	647	647
5 wt%	0.4 wt%	16	1	0.09	15	0.86	1362	1362

Table 3. Parameters of electrochemical impedance spectra in Figure 5, where the pH of the solution was 10 and the chloride concentration was 3.5 wt%.

Cr Content	LDH-NO ₂ Dosage	Q_f ($\mu\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^n$)	n	R_f ($\text{k}\Omega\cdot\text{cm}^2$)	Q_{dl} ($\mu\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^n$)	n	R_{ct} ($\text{k}\Omega\cdot\text{cm}^2$)	$R_p = R_f + R_{ct}$ ($\text{k}\Omega\cdot\text{cm}^2$)
0 wt%	0 wt%	141	0.9	0.03	194	0.89	1	1
1 wt%	0 wt%	220	0.89	0.02	276	0.88	2	2
2 wt%	0 wt%	126	0.86	0.6	20	0.87	6	7
5 wt%	0 wt%	29	0.92	208	62	0.99	56	264
0 wt%	0.2 wt%	102	0.95	0.09	84	0.92	2	2
1 wt%	0.2 wt%	99	0.93	0.1	58	0.9	2	2
2 wt%	0.2 wt%	4	0.76	0.02	62	0.89	30	30
5 wt%	0.2 wt%	2	0.56	0.04	24	0.94	351	351
0 wt%	0.4 wt%	41	0.92	103	28	0.81	68	171
1 wt%	0.4 wt%	38	0.92	98	34	0.8	75	173
2 wt%	0.4 wt%	35	0.92	232	0.5	0.38	0	232
5 wt%	0.4 wt%	16	0.99	0.1	16	0.83	466	466

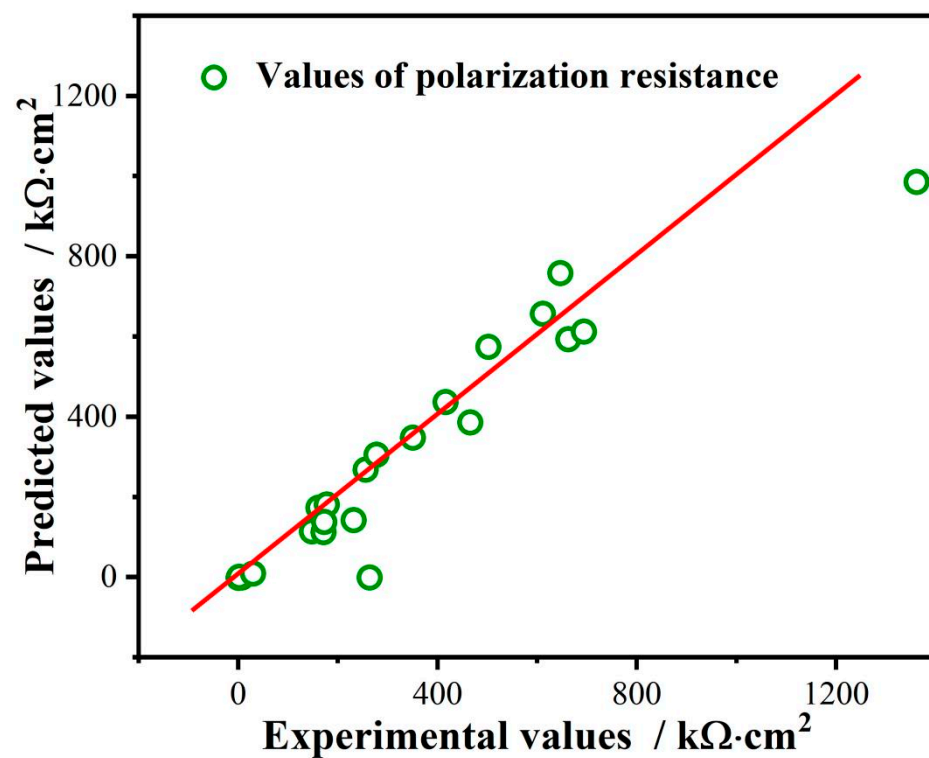


Figure 7. The correlation between the measured polarization resistance (R_p) in Tables 2 and 3 and the predicted R_p from Figure 3.

4. Conclusions

Based on a data-driven research approach, this study employed machine learning algorithms to develop a quantitative predictive model for assessing the correlations between Cr content in steel reinforcement, LDH-NO₂ dosage, concrete chloride concentration, pH value, and the polarization resistance of steel reinforcement. Unlike traditional experimental methods focusing on single control factors, the robust data processing capabilities of machine learning enable rapid analysis of multi-factor interactions affecting steel reinforcement's polarization resistance. It also provides more precise and efficient predictions of the corrosion rate of steel reinforcement under the combined influence of these factors compared to traditional methods. This approach better reflects real-world engineering conditions in steel reinforcement service. The precise and efficient predictive model offers quantitative guidance for selecting alloy elements and corrosion inhibitors in diverse en-

vironments, introducing novel methodologies and perspectives to corrosion research in steel reinforcement.

- (1) The Gaussian kernel support vector machine model (SVR.rbf), obtained through data processing and the analysis and evaluation of machine learning models, exhibited excellent predictive accuracy and stability. The correlation coefficient between the prediction results and experimental values of polarization resistance of the steel reinforcement exceeded 0.85. This provides an accurate and efficient technical method for the prediction of polarization resistance under multi-factor coupling.
- (2) By means of the generalization prediction performance of machine learning models, they provide quantitative reference results for steel reinforcement composition design and corrosion inhibitor selection under actual service conditions. The addition of 1 wt% Cr to steel slightly increases its polarization resistance. However, when the Cr content reaches 3 wt%, the polarization resistance of the steel reinforcement increases significantly; when the Cr content reaches 5 wt%, in the range of pH 12.5~9.5 and containing 0~3.5 wt% chloride, the steel reinforcement's corrosion is essentially negligible.
- (3) The addition of the corrosion inhibitor LDH-NO₂ to concrete gradually reduces the corrosion rate of the steel reinforcement. Adding 0.2 wt% LDH-NO₂ in the environment has a similar effect to adding 3 wt% Cr in the steel reinforcement, while adding 0.5 wt% LDH-NO₂ is comparable to adding 4 wt% Cr.
- (4) The synergistic use of Cr and LDH-NO₂ is more effective in the inhibition of steel reinforcement corrosion than their individual use. With a Cr content of 3 wt% and an LDH-NO₂ concentration of 0.5 wt%, it can be ensured that the steel reinforcement's corrosion is negligible in the range of pH 12.5~9.5 and containing 0~3.5 wt% chloride.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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Appendix A

Table A1. Training data: correlations between Cr content in steel, LDH-NO₂ dosage, chloride concentration in concrete, environmental pH value in pore solution, and polarization resistance of steel reinforcement in the simulated concrete pore solution.

Cr Content (wt%)	LDH-NO ₂ Dosage (wt%)	Cl [−] Concentration (wt%)	pH Value	Polarization Resistance (kΩcm ²)	Ref.
0	0	0	13.3	75	[20]
0	0	0	13.3	262	[20]
0	0	0	12.5	1000	[17]
0	0	0	13.5	604	[17]
0	0	0	12.0	457	[20]
0	0	0	10.5	591	[20]
0	0	0	9.0	433	[20]

Table A1. Cont.

Cr Content (wt%)	LDH-NO ₂ Dosage (wt%)	Cl [−] Concentration (wt%)	pH Value	Polarization Resistance (kΩcm ²)	Ref.
0	0	0	13.5	344	[20]
0	0	0	12.0	311	[20]
0	0	0	10.5	42	[20]
0	0	0	9.0	10	[20]
0	0	0.117	12.5	400	[21]
0	0	0.234	12.5	260	[21]
0	0	0.351	12.5	6	[21]
0	0	0.468	12.5	5	[21]
0	0	0.585	12.5	3	[21]
0	0	0.819	12.5	2	[21]
0	0	0.936	12.5	0.8	[21]
0	0	1.000	12.5	60	[21]
0	0	1.000	12.5	70	[21]
0	0	1.170	12.5	0.6	[21]
0	0	2.530	12.5	238	[22]
0	0	2.925	12.5	0.6	[21]
0	0	5.850	12.5	0.8	[21]
0	0	5.850	12.5	1	[21]
0.08	0	0	12.6	867	[7]
0.08	0	0.200	12.6	839	[7]
0.08	0	0.300	12.3	679	[7]
0.08	0	0.400	12.6	813	[7]
0.08	0	0.450	12.2	603	[7]
0.08	0	0.600	11.9	871	[7]
0.08	0	0.750	11.7	2	[7]
0.08	0	0.800	12.6	578	[7]
0.08	0	0.900	10.9	1	[7]
0.08	0	1.000	12.6	400	[7]
0.08	0	1.200	12.6	236	[7]
0.08	0	1.200	10.1	2	[7]
0.08	0	1.350	9.2	2	[7]
0.08	0	1.400	12.6	186	[7]
0.08	0	1.500	8.8	2	[7]
0.08	0	1.650	8.4	2	[7]
0.86	0	0	12.5	1800	[18]
0.86	0	0.117	12.5	2000	[18]
0.86	0	0.234	12.5	1000	[18]
0.86	0	0.351	12.5	8	[18]
0.86	0	0.468	12.5	7	[18]
0.86	0	0.585	12.5	12	[21]
0.86	0	0.819	12.5	4	[18]
0.86	0	0.936	12.5	2	[18]
0.86	0	1.000	12.5	90	[18]
0.86	0	1.000	12.5	240	[18]
0.86	0	1.170	12.5	1	[18]
0.86	0	2.925	12.5	0.7	[21]
0.86	0	5.850	12.5	2	[21]
0.86	0	5.850	12.5	1.5	[21]
1.00	0	3.530	12.5	393	[19]
1.50	0	0	12.6	963	[19]
1.50	0	1.000	12.6	618	[19]
1.50	0	2.000	12.6	508	[19]
1.50	0	2.200	12.6	476	[19]
1.50	0	2.600	12.6	348	[19]
1.50	0	2.800	12.6	211	[19]

Table A1. Cont.

Cr Content (wt%)	LDH-NO ₂ Dosage (wt%)	Cl [−] Concentration (wt%)	pH Value	Polarization Resistance (kΩcm ²)	Ref.
1.50	0	3.000	12.6	161	[19]
3.00	0	4.530	12.5	650	[19]
5.06	0	1.000	12.6	1529	[19]
5.06	0	2.000	12.6	1238	[19]
5.06	0	3.000	12.6	1130	[19]
5.06	0	4.000	12.6	1000	[19]
5.06	0	5.000	12.6	800	[19]
5.06	0	6.000	12.6	600	[19]
5.06	0	7.000	12.6	400	[19]
5.06	0	7.200	12.6	310	[19]
5.06	0	7.400	12.6	170	[19]
5.06	0	7.600	12.6	146	[19]
5.73	0	0	12.5	3000	[18]
5.73	0	0.117	12.5	700	[18]
5.73	0	0.234	12.5	700	[18]
5.73	0	0.351	12.5	800	[18]
5.73	0	0.468	12.5	550	[18]
5.73	0	0.585	12.5	2353	[18]
5.73	0	0.819	12.5	1000	[18]
5.73	0	0.936	12.5	260	[18]
5.73	0	1.170	12.5	260	[18]
5.73	0	2.925	12.5	260	[18]
5.73	0	5.850	12.5	50	[18]
5.73	0	5.850	12.5	9	[18]
6.00	0	0	13.3	447	[9]
6.00	0	0	13.3	2067	[9]
10.36	0	0	9.0	2673	[16]
10.36	0	0	9.0	2055	[20]
10.36	0	0	10.5	2284	[16]
10.36	0	0	10.5	979	[20]
10.36	0	0	12.0	1770	[16]
10.36	0	0	12.0	481	[20]
10.36	0	0	13.3	1305	[16]
10.36	0	0	13.3	388	[20]
0.08	0.5	0.300	12.0	1148	[15]
0.08	0.5	0.450	11.5	1023	[15]
0.08	0.5	0.600	11.0	1004	[15]
0.08	0.5	0.750	10.7	839	[15]
0.08	0.5	0.900	10.7	935	[15]
0.08	0.5	1.200	10.6	974	[15]
0.08	0.5	1.350	10.6	947	[15]
0.08	0.5	1.500	10.6	134	[15]
0.08	0.5	1.650	10.0	31	[15]

Table A2. Training data after re-cleaning: correlations between Cr content in steel, LDH-NO₂ dosage, chloride concentration in concrete, environmental pH value in pore solution, and polarization resistance of steel reinforcement in the simulated concrete pore solution.

Cr Content (wt%)	LDH-NO ₂ Dosage (wt%)	Cl [−] Concentration (wt%)	pH Value	Polarization Resistance (kΩcm ²)
0.08	0	0	12.6	867
0.08	0	0.2	12.6	839
0.08	0	0.4	12.6	813
0.08	0	0.8	12.6	578

Table A2. Cont.

Cr Content (wt%)	LDH-NO ₂ Dosage (wt%)	Cl [−] Concentration (wt%)	pH Value	Polarization Resistance (kΩcm ²)
0.08	0	1.0	12.6	400
0.08	0	1.2	12.6	236
0.08	0	1.4	12.6	186
1.5	0	0	12.6	963
1.5	0	1.0	12.6	618
1.5	0	2.0	12.6	508
1.5	0	2.2	12.6	476
1.5	0	2.4	12.6	424
1.5	0	2.6	12.6	348
1.5	0	2.8	12.6	211
1.5	0	3.0	12.6	161
5.06	0	1.0	12.6	1529
5.06	0	2.0	12.6	1238
5.06	0	3.0	12.6	1130
5.06	0	4.0	12.6	1000
5.06	0	5.0	12.6	800
5.06	0	6.0	12.6	600
5.06	0	7.0	12.6	400
5.06	0	7.2	12.6	310
5.06	0	7.4	12.6	170
5.06	0	7.6	12.6	146
0.08	0.5	0.3	12.0	1148
0.08	0.5	0.45	11.5	1023
0.08	0.5	0.6	11.0	1004
0.08	0.5	0.75	10.7	839
0.08	0.5	0.9	10.7	935
0.08	0.5	1.2	10.6	974
0.08	0.5	1.35	10.6	947
0.08	0.5	1.5	10.6	134
0.08	0.5	1.65	10.0	31
0.08	0	0.3	12.3	679
0.08	0	0.45	12.2	603
0.08	0	0.6	11.9	871
0.08	0	0.75	11.7	1.672
0.08	0	0.9	10.9	1.362
0.08	0	1.2	10.1	1.846
0.08	0	1.35	9.2	1.822
0.08	0	1.5	8.8	2.495
0.08	0	1.65	8.4	1.556

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