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# Corrosion Behavior of Cr-bearing Corrosion Resistant Rebar in Concrete with Chloride Ion Content

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**Abstract**

Conventional studies have focused on the reduction in the water-cement ratio, the use of various admixtures, etc., to ensure the durability of reinforced concrete structures against such deterioration factors as carbonation and chloride attack. However, improvement in the concrete quality alone is not considered sufficient or realistic for meeting the recent demand for a service life of over 100 years. This study intends to improve the durability of reinforced concrete structures by improvement in the reinforcing steel, which has remained untouched due to cost problems, through subtle adjustment of the steel components to keep the cost low.

As a fundamental study on the performance of Cr-bearing rebars in steel reinforced concrete structures exposed to corrosive environments, The test specimens were made by installing 8 types of rebars in concretes with a chloride ion content of 0.3, 0.6, 1.2, 2.4 and 24kg/m$^3$. Corrosion accelerated curing were then conducted with them. The corrosion resistance of Cr-bearing rebars was examined by measuring crack widths, half-cell potential, corrosion area and weight loss after 155 cycles of corrosion-accelerating curing.

The results of the study showed that the corrosion resistance increased as the Cr content increased regardless of the content of chloride ions, and that the Cr-bearing rebars with a Cr content of 5% and 9% showed high corrosion resistance in concretes with a chloride ion content of 1.2 and 2.4kg/m$^3$, respectively.

*Keywords: cr-bearing rebar, corrosion resistance, corrosion area, weight loss*

## 1. INTRODUCTION

Steel reinforced concrete is widely used for various types of structures due to its high durability, which is deemed semi-permanent, and its cost-effectiveness. However, a reinforced concrete structure cannot function soundly throughout its required service life unless it is appropriately designed and executed for the specific service conditions (Matsushita, 1999). The corrosion of reinforced concrete structures demonstrates very complicated forms of deterioration intermingled together but all pointing to a decrease in the durability of reinforced concrete structures by the corrosion of reinforcing bars (Lee, 2003). For this reason, many studies have been conducted to discover the best method of preventing corrosion in reinforcing bars. However, most of them have been disproportionately concentrated on the improvement of concrete quality such as the increase in concrete cover thickness, optimization of water-to-cement ratio or the addition of corrosion-inhibiting materials. Nevertheless, improvement in the concrete quality alone is not considered sufficient or realistic for meeting the recent demand for a service life of over 100 years. In America and Europe, epoxy-coated rebars and stainless steel rebars with high corrosion resistance have already been applied to many concrete structures, such as road bridges, elevated highways, tunnels, parking garages, residential buildings, and port facilities (Smith, 1999; Rostam, 2003), but epoxy-coated rebars have certain drawbacks. They cause losses in the bond strength with concrete and are prone to damage to epoxy coating during transportation, bending, and fabrication, thereby being rendered vulnerable to macrocell corrosion (Treece, 1989; Miura, 1997). On the other hand, stainless steel rebars (e.g., type 316LN: 16%Cr-12%Ni-2%Mo-0.2%N) have shown very good performance in highly saline environments. Type 304 (18%Cr-8%Ni) stainless steel rebars used for a concrete pier exposed to a tropical marine environment for 60 years showed little corrosion damage (Borges, 2002). Despite its excellent corrosion resistance, stainless steel has not been widely used, due to the high cost resulting from costly elements such as chromium (Cr) and nickel (Ni), which also require additional manufacturing steps as compared with other general steel manufacturing processes. However, it is worthwhile to investigate corrosion-resistant rebars that eventually lead to a lower life cycle cost in view of the ever-increasing maintenance cost for reinforced concrete structures. If low-cost stainless steel rebars with lower Cr and Ni contents (hereafter referred to as Cr-bearing rebar) are made available, then the excessive concrete cover thickness can be reduced and the regulation on the water-to-cement ratio will become less strict, at which time the life time of reinforced concrete structures can be extended by using such highly cost-effective corrosion-resistant rebars that remain unaffected by corrosion in corrosive environments.

As a fundamental study on the performance of Cr-bearing rebars in steel reinforced concrete structures exposed to corrosive environments, their corrosion resistance was investigated in simulated concrete pore solutions and concrete specimens containing chloride ions.

## 2. OUTLINE OF EXPERIMENT

Eight types of reinforcing bars with different Cr contents were embedded in concretes with a chloride ion content of 0.3, 0.6, 1.2, 2.4 and 24kg/m$^3$ so as to induce microcell corrosion. Four bars, two bars each of two types, were arranged in two layers in each specimen, with the bars of the same type being placed on the same side with respect to the direction of concrete placement as shown in Figure 1. After being seal-cured for 7 days, the specimens were demolded and air-cured for 7 days in a thermo-hygrostatic room at 20 ± 3°C and 50 ± 5% R.H. The specimens were then subjected to high temperature /humidity and low temperature/humidity cycles to accelerate corrosion of reinforcement. Each cycle consisted of a high temperature/humidity phase at 60°C and 95% R.H. for one day and a low temperature/humidity phase at 30°C and 50% R.H. for one day. The half-cell potential was measured at the end of every 5 cycles. Additionally, the corrosion area and the weight loss of reinforcing bars taken out of cleft specimens were measured at the end of 50, 65 and 155 cycles. Measurement after 50 and 65 cycles of corrosion-accelerating curing was decided because these were times when a 0.3mm crack was observed on the surfaces of specimens with a chloride ion content of 2.4 $kg/m^3$ and 1.2$kg/m^3$, respectively, in which SD345 rebars were installed. Also, measurement after 155 cycles was decided because this was the time when a 0.1mm crack was found on the surfaces of specimens with a chloride ion content of 0.6$kg/m^3$ containing SD345 bars. Table 1 and Table 2 give the material properties and the mixture compositions of concrete, respectively. Also, a total of 8 types of rebar specimens were used in this experiment, including SD345 conforming to JIS G 3112 (Steel bars for concrete reinforcement), 6 types of Cr-bearing rebars with different Cr contents and SUS304 stainless steel rebars. Note that the rebars were 13mm in diameter with the oxidized coating being removed. The steel compositions are the same as Table 3.

Table 1. Material properties

| Materials | Kind/Characteristics |
|---|---|
| Cement | Ordinary Portland Cement |
| Water | Potable |
| Fine Aggregate | Crushed Sand and Land Sand/Density=2.52 $ton/m^3$, Absorption=1.42 %, Fineness Modulus=2.73 % |
| Coarse Aggregate | Crushed Stone (Sand Stone)/Density=2.64 $ton/m^3$, Absorption=0.59 %, Fineness Modulus=6.75 % |
| Chemical Admixture | Air Entraining and High-range Water Reducing Agents |
| NaCl | First class reagent |

Table 2. Mixture compositions of concret

| Chloride ion ($kg/m^3$) | W/C (%) | S/A (%) | Unit weight ($kg/m^3$) | | | |
|---|---|---|---|---|---|---|
| | | | W | C | S | G |
| 0.3 | | | | | | |
| 0.6 | | | | | | |
| 1.2 | 60 | 46 | 185 | 285 | 798 | 954 |
| 2.4 | | | | | | |
| 24 | | | | | | |

Table 3. Chemical compositions of steel rebars, mass%

| Steel | C | Si | Mn | P | S | Cr | Ni | Mo |
|---|---|---|---|---|---|---|---|---|
| SD345 | 0.2280 | 0.31 | 1.34 | 0.029 | 0.020 | 0.084 | 0.04 | 0.016 |
| 0Cr | 0.0120 | 0.32 | 0.50 | 0.031 | 0.006 | 0.005 | 0.01 | 0.001 |
| 5Cr | 0.0150 | 0.28 | 0.53 | 0.027 | 0.006 | 5.020 | 0.01 | 0.001 |
| 9Cr | 0.0107 | 0.28 | 0.53 | 0.028 | 0.006 | 9.140 | 0.01 | 0.001 |
| 11Cr | 0.0117 | 0.28 | 0.53 | 0.028 | 0.004 | 11.00 | 0.01 | 0.001 |
| 13Cr | 0.0117 | 0.28 | 0.53 | 0.028 | 0.004 | 13.05 | 0.01 | 0.002 |
| 16Cr | 0.0113 | 0.29 | 0.53 | 0.027 | 0.004 | 15.98 | 0.01 | 0.002 |
| SUS304 | 0.0630 | 0.31 | 1.01 | 0.026 | 0.006 | 18.36 | 8.28 | 0.053 |

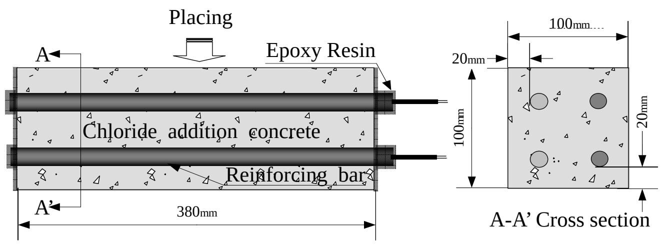


Figure 1. Details of test specimen.

## 3. EXPERIMENT PROCEDURE

### (1) Corrosion Accelerated Curing

Following the above-mentioned curing process, the acceleration of corrosion for each specimen was achieved by repeated high and low temperature curing as well as wet and dry curing. Each curing cycle consisted of one-day high temperature/humidity (temp. 60°C, humidity 95%) curing and one-day low temperature/humidity (temp. 30°C, humidity 50%) curing. Moisture is supplied to the specimen in a high temperature/humidity, and the specimen is aerated in a low temperature/humidity.

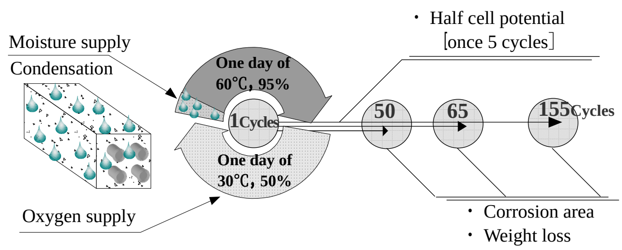


Figure 2. Cycles of wetting and drying.

### (2) Crack Width

Each time the corrosion accelerated curing increased by 5 cycles, the crack width created on the concrete surface was measured using a crack scale.

### (3) Half-cell Potential

The half-cell potential was measured along the bars across the cover concrete at 50mm intervals using saturated copper-copper sulfate electrodes, and the average of the seven measurements was determined for each bar. On the day before testing, specimens were immersed in water for three hours, wrapped in a wet cloth, and stored in a plastic bag until testing to adjust the moisture content.

(4) Corrosion Area and Weight Loss

The corrosion areas and weight losses were measured using reinforcing bars chipped out of cleft specimens after 50, 65, and 155 cycles of corrosion-accelerating curing. The measurement for specimens with a chloride ion content of 0.3kg/m$^3$ was omitted at 65 cycles, as no appreciable progress in corrosion was anticipated for these specimens between 50 and 65 cycles. The corrosion area was calculated using an automatic area measuring software after copying the corroded areas of rebars using a transparent sheet and blacking the areas. The weight losses by corrosion were measured in accordance with the method of evaluating corrosion of reinforcing steel in

$$\Delta W = \frac{(Wo - W) - Ws}{Wo} \times 100 \qquad (1)$$

where

$\Delta W$ = weight loss (%)

$Wo$ = reinforcing bar mass before the rust removing process (g)

$W$ = reinforcing bar mass after the rust removing process (g)

$Ws$ = mass of non-corroded part dissolved from the bar (g)

Figure 3. Cr-bearing Corrosion Resistant Rebar.

Figure 4. Corrosion Accelerated Curing ［Chamber］.

Figure 5. Half-cell Potential ［adjustment the moisture content］.

Figure 6. Operation to take out the rebar from the concrete.

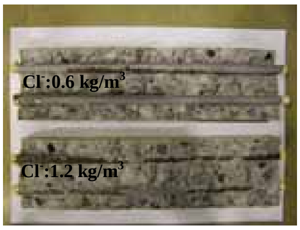


Figure7. Degree of corrosion of rebar［SD345,50Cycle］.

Figure 8. Remove of rust.

concrete in the "Test methods and standards related to corrosion of concrete structures (draft)" established by the Japan Concrete Institute (Japan Concrete Institute, 1987). SD345, 0Cr and 5Cr rebars were immersed in a 10% aqueous solution of diammonium citrate, while rebars with a Cr content exceeding 5% were immersed in a 15% aqueous solution of nitric acid, to remove rust. The mass of the bars were then measured to the nearest 0.01g using an electronic balance. The weight losses were calculated using Equation (1).

## 4. RESULT AND DISCUSSION

### (1) Crack Width

Figure 9 shows the width change of cracks over time for chloride ion content that were created on the surface of the concrete in which different types of rebars were buried. Figure 9 also indicates that for all types of rebars the crack width tends to be greater for the concrete that have higher chloride ion content. For the concrete with chloride ion content less than 1.2kg/m$^3$, hair-line cracks were observed only in the concrete with SD345 rebar and 0Cr rebar having no Cr content. For the concrete with chloride ion content of 2.4kg/m$^3$, hair-line cracks were found not only in the concrete with SD345 rebar and 0Cr rebar but also in the concrete with 5Cr rebar with 5% Cr content. However, no cracks were observed on the surface of the concrete with Cr-bearing corrosion resistant rebar having a Cr content of more than 9%. In addition, for the concrete with chloride ion content of 24kg/m$^3$, cracks were observed on the surface of the concrete where corrosion was observed as well as on the surface of the concrete with Cr-bearing

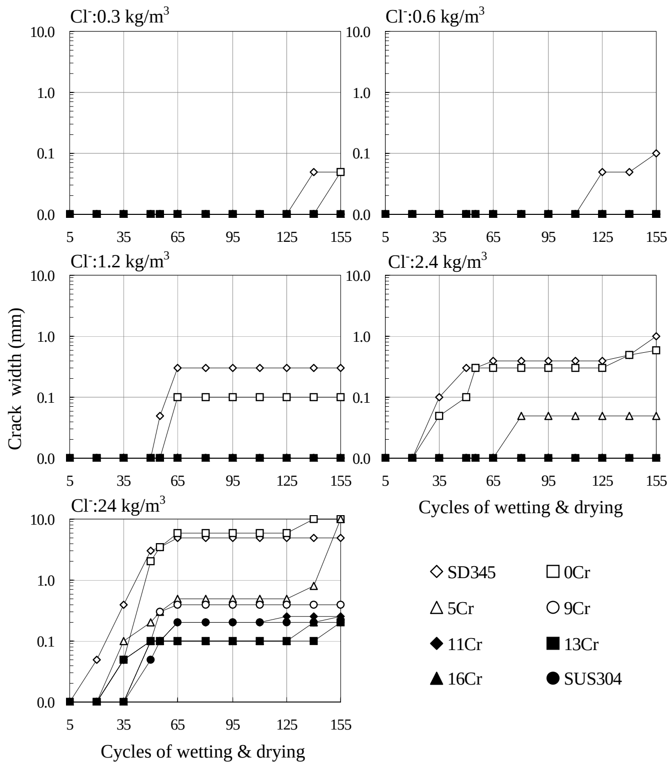


Figure 9. Change in crack width.

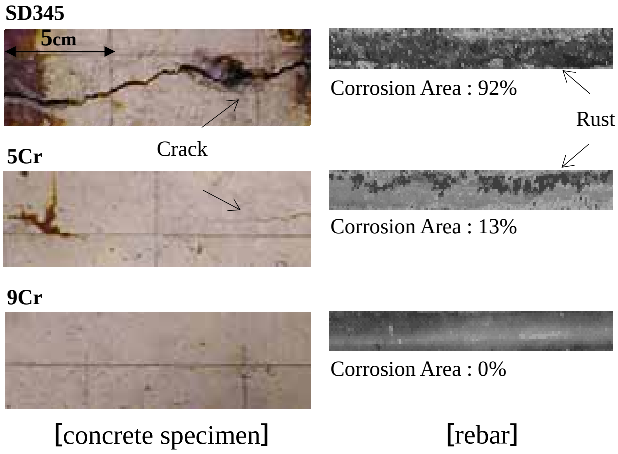


Figure 10. Crack and Degree of corrosion. [155 Cycle, 2.4kg/m$^3$]

corrosion resistant rebar having a Cr content of more than 11% where no corrosion was found. It is hardly believable that these cracks were created due to the corrosion of the rebar. However, it is assumed that the cracks were caused by the weakening of the concrete containing a large amount of chloride due to corrosion accelerated curing. As for the 0Cr rebar, crack width is smaller than that of SD345. The reason is corrosion product of the 0Cr rebar is smaller than corrosion product of SD345 because the carbon content of the 0Cr rebar is lower than that of SD345. Figure 10 shows the crack widths and degree of corrosion of rebar at the 155cycle that were created on the concrete specimens with chloride ion content of 2.4kg/m$^3$ in which SD345 rebar, 5Cr rebar and 9Cr rebar were installed.

(2) Half-cell Potential

Figure 11 shows the changes in the half-cell potential of reinforcing bars with different chloride ion contents related to acceleration cycles. The bold lines in the graphs indicate a potential value of -0.35V (vs CSE), which can be regarded as corroded with 90% certainty according to the corrosion criteria of ASTM C 876-80 (ASTM C 876-80, 1981). Figure 11 reveals that bars with a higher Cr content demonstrate less negative half-cell potentials when compared under the same chloride conditions, owing to the strong passive film formed on the rebar surface by the reaction between chromium and oxygen (Stainless steel association, 1984; Uhlig, 1953).

In the case of concretes with a chloride ion content of 0.3kg/m$^3$ and 0.6kg/m$^3$, the half-cell potentials of SD345 and 0Cr rebars are in the proximity of -0.35V, the corrosion threshold by ASTM. However, the half-cell potentials of Cr-bearing rebars with a Cr content of 5% or more are less negative than -0.35V. In the case of concretes with a chloride ion content of 1.2kg/m$^3$ and 2.4kg/m$^3$, the half-cell potentials of Cr-bearing rebars with a Cr content of 5% or more and 9% or more remain less negative than -0.35 V up to 155 cycles but tend to approach -0.35 V toward 155 cycles. In the case of concrete with a chloride ion content exceeding 24kg/m$^3$, the half-cell potential of all rebars excepting SUS304 is more negative than -0.35 V. According to these results, it can be said that rebars with a Cr content of 5% or more and 9% or more are corrosion resistant in concrete with a chloride ion content of 1.2 kg/m$^3$ and 2.4kg/m$^3$, respectively. This agrees with the test results in simulated concrete pore solutions showing that steel with a Cr content of 5% or more was resistant to corrosion in a simulated concrete pore solution with a pH value of 12.5 and NaCl concentration of 1.07% corresponding to concrete with a chloride content of 1.2 kg/m$^3$. However, despite the corrosion resistance of 16Cr steel observed in a simulated concrete pore solution with a pH value of 12.5 and NaCl concentration of 21.4%, the measured half-cell potential of 16Cr steel in concrete with a chloride ion concentration of 24kg/m$^3$, which corresponds to the said solution, is more negative than -0.35 V. Nevertheless, 16Cr steel exhibited corrosion resistance in terms of corrosion area ratio and weight loss to be discussed later in this paper.

Since the criteria of ASTM C 876 are intended for corrosion of carbon steel in structures subjected to chloride attack, new criteria should be established for corrosion of Cr steel, which shows polarization behavior different from that of carbon steel. Careful judgment based on sufficient research data is necessary for such establishment, demanding extensive data accumulation.

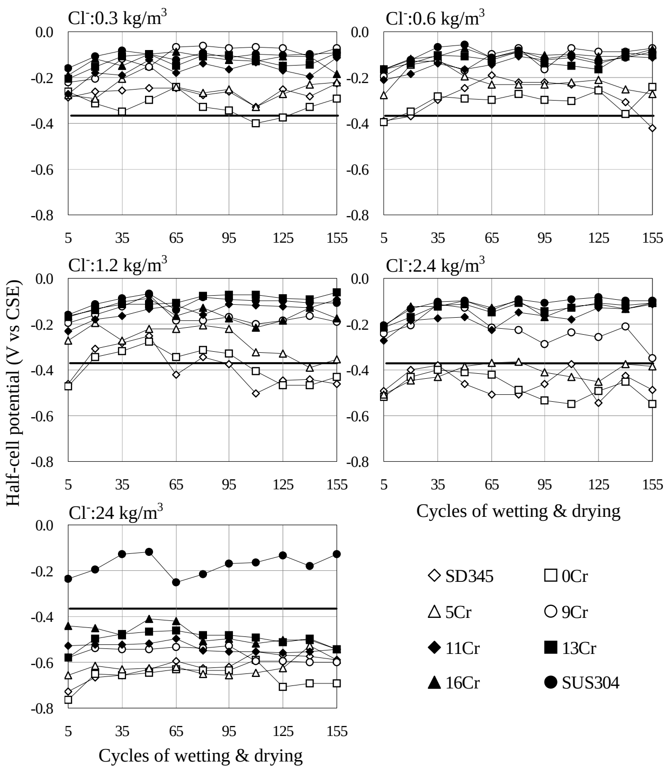


Figure 11. Change in half-cell potential.

(3) Corrosion Area

Figure 12 shows the changes in the corrosion areas of various types of rebars by chloride ion content related to the accelerated corrosion cycles. This figure reveals that the corrosion area tends to decrease as the Cr content increases regardless of the chloride ion content. When compared among the same steel type, the corrosion area increases as the chloride ion content increases.

In concretes with a chloride ion content of 0.3kg/m$^3$ and 0.6kg/m$^3$, corrosion occurred only on SD345 and 0Cr rebars, and the corrosion area tended to slowly increase as the number of cycles increased. When the chloride ion content was 1.2kg/m$^3$, which is the limit of chloride content for corrosion of the carbon steel rebar set out by the Japan Society of Civil Engineers (Japan Society of Civil Engineers, 2000), no appreciable corrosion was observed on Cr-bearing rebars with a Cr content of 5% or more up to 155 cycles.

With a chloride ion content of 2.4kg/m$^3$, the corrosion area ratio on SD345 and 0Cr steel rapidly increased by 65 cycles and approached 100% by 155 cycles. However, it remained around 20% on 5Cr steel at 65 cycles with no further increases thereafter. 9Cr steel also showed no appreciable corrosion until 155 cycles.

When the chloride ion content was as high as 24kg/m$^3$, the corrosion area ratio rapidly increased even on 5Cr steel. It also tended to progressively increase on 9Cr and 11Cr as the number of cycles increased. However, no appreciable corrosion was observed on Cr-bearing rebars with a Cr content of 13% or more in concrete with such a high chloride ion content.

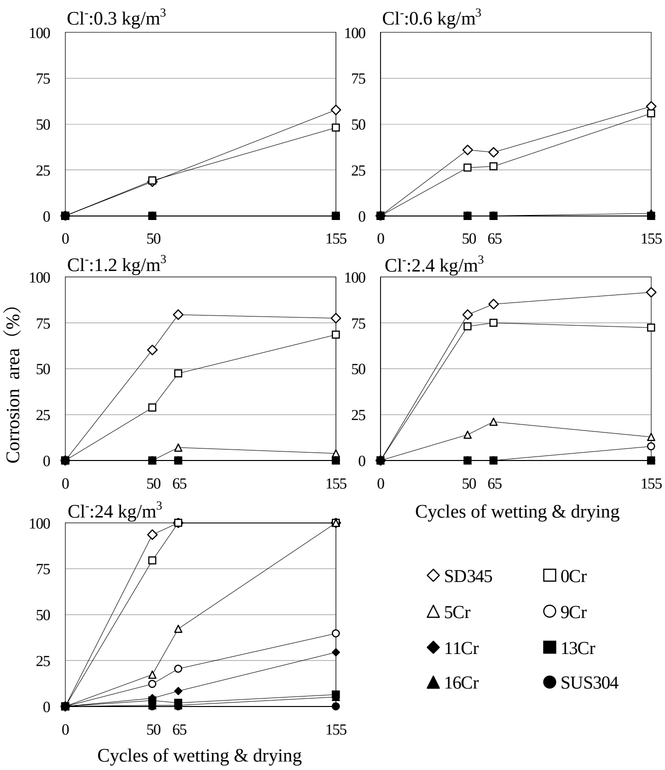


Figure 12. Change in corrosion area.

(4) Weight Loss

Figure 13 shows the weight losses of various types of rebars by chloride ion content related to accelerated corrosion cycles. This figure reveals that the weight losses of reinforcing bars tend to decrease as their Cr content increases when the chloride ion content of concrete is the same. Also, the weight losses increase as the chloride ion content increases regardless of the rebar type. Such a tendency is conspicuous with SD345 and 0Cr bars. The weight losses of these bars, which are less than 3% with a chloride ion content of 0.3kg/m$^3$ and 0.6kg/m$^3$, increase more rapidly with a higher chloride ion content. Such a phenomenon becomes more conspicuous as the number of cycles increases. In concrete with a chloride ion content of 1.2kg/m$^3$, the weight losses of SD345 increase as the number of cycles increases, but those of steels with a Cr content of 5% or more were nearly zero up to 155 cycles. When the chloride ion content is 2.4kg/m$^3$, even 5Cr steel shows a tendency toward gradual increases in the weight losses as the number of cycles increases, but the losses are marginal with a Cr content of 9% or more. It should be noted that with a Cr content of 13% or more, no appreciable weight losses are measured even in concrete with a chloride content of 24kg/m$^3$.

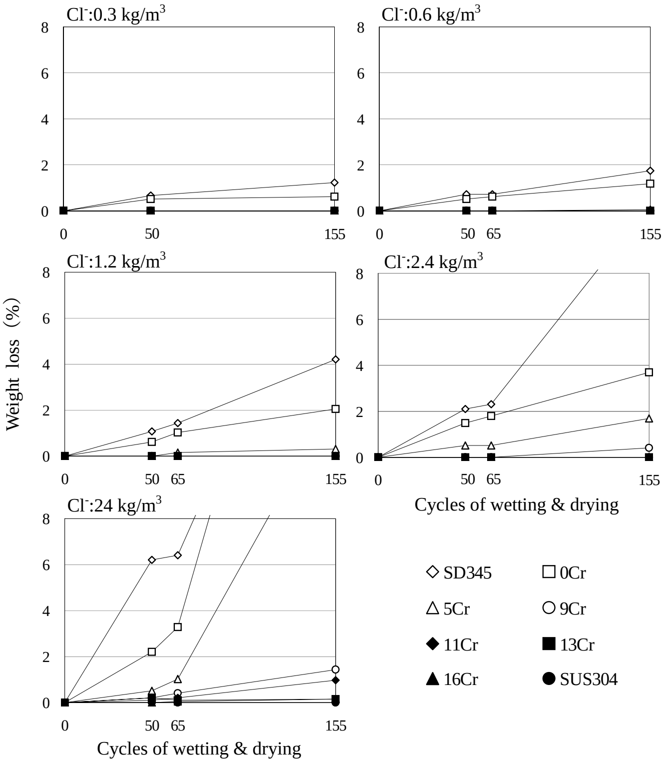


Figure 13. Change in weight loss.

In view of the results of these tests for corrosion area and weight loss up to 155 cycles of accelerated corrosion, Cr-bearing rebars with a Cr content of 5% or more and 9% or more are found to resist corrosion in concrete with a chloride content of up to 1.2kg/m$^3$ and 2.4kg/m$^3$, respectively. In concrete with a chloride content of 24kg/m$^3$, a Cr content of 13% or more is expected to resist corrosion.

(5) Average Corrosion Rate

Figure 14 shows the relationship between the chloride ion content and the average corrosion rate by steel type. The average corrosion rates are the averages of the corrosion rates determined at 50, 65 and 155 cycles of corrosion-accelerating curing. The average corrosion rate increases along with the increase in the chloride ion content irrespective of the steel type.

The slopes of the corrosion rates of SD345 and 0Cr steel tended to become steeper when the chloride ion content exceeded 1.2kg/m$^3$, with the rate of SD345 with a higher carbon content being higher than that of 0Cr. On the other hand, the corrosion rate of 5Cr steel with a Cr content of 5% remains marginal up to a chloride ion content of 1.2 kg/m$^3$ but progressively increases as the chloride content increases toward 24kg/m$^3$. However, for 9Cr rebars, infinitesimal average corrosion rates were observed even in the concrete with a chloride ion content of 24kg/m$^3$. The corrosion rate of rebars with a Cr content of 13% or more was particularly low, being virtually 0%. Figure 15 shows the effects of the chloride ion content of concrete and the Cr content of reinforcement on the average corrosion rate of reinforcement. When the environmental conditions of a building are clearly related to the conditions of accelerated corrosion in this study in the future, the spectrum shown in Figure 15 will allow the designer to select steel reinforcement with an optimum Cr content in consideration of the target service life of the building and the chloride ions to be present in the concrete.

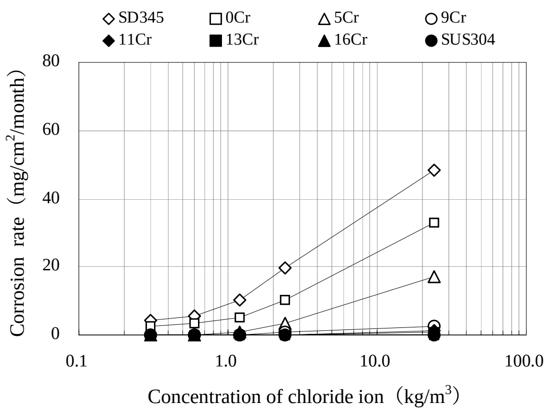


Figure 14. Change in average corrosion rate.

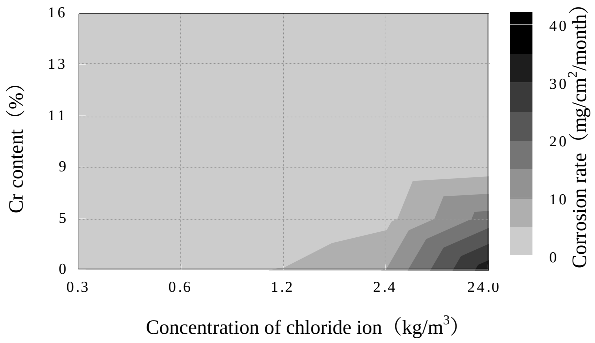


Figure 15. Effect of the chloride ion content and Cr content to the average corrosion rate.

## 5. CONCLUSIONS

For the purpose of developing Cr-bearing rebars that can be used under corrosive environments, experiments were conducted on the corrosion resistance of Cr-bearing rebars in simulated concrete pore solutions and concrete specimens containing chloride ions.

The following was obtained from these experiments:

1. Irrelevant of the chloride content, the corrosion area and the weight loss by corrosion were low when the Cr content was high. From this it is considered that the corrosion resistance against the chloride has improved due to the formation of passive film by chromium.
2. The Cr content required for corrosion resistance was 5% or more and 9% or more when the chloride ion contents of the concrete were 1.2kg/m$^3$ and 2.4kg/m$^3$, respectively.
3. For concrete with a chloride content of 24kg/m$^3$, Cr-bearing rebars with a Cr content of 13% or more are expected to resist corrosion.

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