Threshold of the chloride to hydroxide ions ratio in relation to steel reinforcement corrosion

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Abstract. A simple method for determining the corrosion dependence of steel reinforcement on the content of chloride and hydroxide ions is described. Steel test specimens were immersed for nine months in solutions with 0.03%, 0.3% and 3% NaCl with increasing concentrations of hydroxide ions, and pH of 8.5 to 13. The test specimens were cleaned of corrosion products and weighed at given time intervals of one month. The dependence of mass loss expressed as a percentage of the concentration of chloride and hydroxide ions was determined. The concentration threshold of the cCl⁻/cOH⁻ ratio of 0.5 was evaluated from the results. Higher values of this ratio resulted in the formation of corrosion products on the surface of the test specimens.

1. Introduction

Chloride corrosion of steel reinforcement in concrete is a problem not only in coastal regions but also in regions where winter maintenance of roads with de-icing salts is carried out. Corrosion of steel reinforcement can be derived from the Pourbaix diagram, which maps out possible stable compounds on the Fe surface in aqueous solutions [1]. The pH values for passive stages of steel reinforcement can be derived. The relation between potential and pH varies in the presence of chlorides. Therefore, it is necessary to find a threshold concentration ratio between chloride and hydroxide ions. High concentration ratios are dangerous for steel reinforcement. Chloride ions can be present in free and bound form in concrete. Free chlorides are present in water-soluble compounds, and these ions participate in corrosion processes.

Numerous authors [2-7] have solved the free chloride concentration to hydroxide ion concentration threshold. Alonso et al. [8] summarised the results of the chloride and hydroxide ion ratio threshold of various authors. The critical value is between 0.12 and 6.0, depending on the environment in which the steel reinforcement is inserted.

The authors [8] based their results on electrochemical measurements of corrosion potential (Ecorr), electrical (Rₑ) and polarisation (Rₚ) resistance. The corrosion current was calculated from the measurement results. They found that steel reinforcement depassivation occurs when the corrosion current is greater than 0.1 \( \mu \text{A/cm}^2 \).

The concentrations of chloride and hydroxide ions in the synthetic concrete pore solution are well defined. The concentration ratio thresholds were measured to be the lowest between 0.25 and 1.09 [2, 3, 9]. Higher threshold of concentration ratios of 6.0 were determined in cement mortars and concretes. Steel reinforcement corrosion in concrete depends on many factors, in particular the porous structure of the concrete, the diffusion coefficient for chlorides, the pH of the pore solution and the moisture of the concrete.
The article is focused on the monitoring of reinforcement corrosion in the form of steel test specimens in synthetic pore solutions with increasing pH and chloride ions and determining the critical concentration ratio of chloride and hydroxide ions via a simple method of steel mass loss.

2. Mechanism of steel reinforcement corrosion
Steel reinforcement in concrete is stored in a high concentration of hydroxide ions (pH ~ 12), which stabilise the phases on steel surface. Reducing the concentration of hydroxide ions below a certain threshold causes corrosion. Corrosion reactions are realised on the local electrodes:

Anodic reaction

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \]

Cathodic reaction

\[ \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2 \text{e}^- \rightarrow 2 \text{OH}^- \]

When chlorides are present, they participate in the corrosion reactions. Their participation in the corrosion process can be described by the following chemical reactions [4]:

\[ \text{Fe}^{2+} + 2 \text{Cl}^- \rightarrow \text{FeCl}_2 \]

\[ \text{FeCl}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2 \text{Cl}^- \]

\[ 6 \text{FeCl}_2 + \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_2\text{O}_4 + 12 \text{H}^+ + 12 \text{Cl}^- \]

Chlorides enter and exit the reaction as Cl\(^-\). The chloride anion can be labelled as a catalyst and can be reused.

3. Materials and methodology
The corrosion attack of steel in chloride solutions prepared with three concentrations of chlorides combined with OH\(^-\) ions in the pH range of 8.5 to 13 was monitored for nine months. The sodium chloride solutions contained 3, 0.3 and 0.03% of NaCl, which correspond to 0.529 mol/l, 0.0529 mol/l and 0.00529 mol/l of chloride anions, respectively. The corrosive solutions were prepared by dissolving NaCl in buffer solutions. To ensure pH stability, a buffer was prepared using boric acid and potassium chloride. This type of buffer maintained the pH stability of the corrosion solution for one month. The chloride content of the buffer was included in the chloride concentration in the corrosion solution. The pH of the corrosion solutions was measured every month. Although the pH was almost unchanged, fresh solutions were prepared each month.

The smooth steel specimens (specification of steel: ZTV d=10 S 235 JRG2 according to EN 10025) of 10 mm diameter and a length of 100 mm were used for the experiments. The test specimens were degreased with an organic solvent prior to immersion into the solutions and weighed. The solutions with the test specimens were placed into 500 ml polyethylene enclosed bottles (Fig. 1). The concentration ratios c(Cl)/c(OH) of the prepared solutions are presented in Table 1.

![Figure 1. Steel test specimens in bottles with corrosion solutions.](image-url)
The steel test specimens were removed from the solution at the selected time intervals (one month), cleaned of corrosion products, dried and weighed. Before removing the corrosion products, the samples were visually evaluated, and their documentation photo was taken. The mass loss was used for calculating the percentage changes of mass in time. From the results of corrosion losses, the threshold values of chloride and hydroxide ions concentration were found.

| pH   | Cl/OH^- 3% sol. of NaCl | Cl/OH^- 0.3% sol. of NaCl | Cl/OH^- 0.03% sol. of NaCl |
|------|-------------------------|---------------------------|----------------------------|
| 8.5  | 167356.0                | 16735.6                   | 1673.6                     |
| 9.0  | 52923.0                 | 5292.3                    | 529.3                      |
| 9.5  | 16735.6                 | 1673.6                    | 167.4                      |
| 10.0 | 5292.3                  | 529.2                     | 52.9                       |
| 10.5 | 1673.6                  | 167.4                     | 16.7                       |
| 11.0 | 529.2                   | 52.9                      | 5.3                        |
| 11.5 | 167.4                   | 16.7                      | 1.7                        |
| 12.0 | 52.9                    | 5.3                       | 0.5                        |
| 12.5 | 16.7                    | 1.67                      | 0.2                        |
| 13.0 | 5.3                     | 0.5                       | 0.1                        |

### 4. Results and discussion

#### 4.1. Visual assessment
Prior to removing the corrosion products, the corrosion rate was visually assessed. The rating was done on a three-point scale:
1. No corrosion (NC).
2. Pitting corrosion at several points (PC).
3. General corrosion on the whole surface (GC).

The results of the visual assessment after nine months are present in Table 2.

| Assessment | pH range for 0.03% NaCl | pH range for 0.3% NaCl | pH range for 3% NaCl |
|------------|-------------------------|------------------------|---------------------|
| NC         | ≥ 12                    | ≥ 12.5                 | -                   |
| PC         | 9 - 11.5                | 9.5 - 12               | 10.5 - 13           |
| GC         | < 8.5                   | 8.5 - 9                | 8.5 - 10            |

The image of the test specimens was documented with photos. The images of the steel specimens after nine months in the chosen corrosion environment are presented in Fig. 2, 3 and 4. There is significant surface corrosion on the whole specimens in solutions with higher concentration of chlorides. The test specimens immersed in 3% NaCl and pH 13 contained only a few small pitting places.

**Figure 2.** Image of steel specimens in 0.03% corrosion solution.
4.2. Determination of threshold concentration ratio $c(\text{Cl})/c(\text{OH})$

The steel mass loss decreases with increasing pH value. The mass loss is significantly reduced in solutions with pH of 12.5: the steel did not corrode in the 0.03% NaCl solution. Results of mass loss vs. pH value are presented in Fig. 5, 6 and 7. Specification 1M to 9M is number of months.
Figure 7. Mass loss vs. pH in 0.03% NaCl solution.

The mass loss results were correlated with the chloride and hydroxide ion ratios. The graphs in Fig. 8, 9 and 10 show the threshold level of the c(Cl⁻)/c(OH⁻) concentration ratio. The NaCl solution (3% concentration) corresponds to a concentration ratio c(Cl⁻)/c(OH⁻) of 5.3 for a pH value of 13. It is a high value of pH. The pitting corrosion was noted on the steel surface in our experiments.

A value of 0.5 was found for the threshold of the c(Cl⁻)/c(OH⁻) concentration for the pH 13 and 0.3% NaCl. For the lowest NaCl concentration of 0.03%, a threshold of 0.5 for pH 12 was found.

Figure 8. Mass loss vs. concentration ratio c(Cl⁻)/c(OH⁻) in 3% NaCl solution.

5. Conclusion
This paper focused on the determination of the threshold value of the concentration ratio c(Cl⁻)/c(OH⁻) via a simple method of mass loss. Corrosion experiments were performed in solutions of three concentrations of NaCl and increasing pH from 8.5 to 13.

The following conclusions can be drawn from the results:
- The concentration of hydroxide ions is the most important factor for steel reinforcement corrosion.
- Steel reinforcement corrosion is dependent on the c(Cl⁻)/c(OH⁻) concentration ratio.
- The threshold value of the c(Cl⁻)/c(OH⁻) ratio for steel reinforced corrosion is 0.5.

In conclusion, when assessing the corrosion of steel reinforcement in concrete, it is necessary to determine both the chloride ion content and the pH value.
Figure 9. Mass loss vs. concentration ratio c(Cl\textsuperscript{-})/c(OH\textsuperscript{-}) in 0.3% NaCl solution.

Figure 10. Mass loss vs. concentration ratio c(Cl\textsuperscript{-})/c(OH\textsuperscript{-}) in 0.03% NaCl solution.

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