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Interactions Between Reinforcement Corrosion and Chloride Ion Diffusion in Mortar

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ABSTRACT

This study explored the diffusion of the chloride ions influenced by the reinforcement corrosion in the mortar. It is believed that, during the corroding process, a small current is generated at the surface of the reinforcement. Such current is supposed to influence the diffusion of the chloride ions, but the relationship between both was not well studied in the literature. In this study, the corroded reinforcements were prepared by applied currents. Reinforced mortar specimens with w/c of 0.6 were then prepared and cured by either salt or fresh water. Results showed that the chloride ion distribution was likely associated with the reinforcement corrosion. During the early hydration, the chloride ions were attracted by the reinforcement corrosion in the specimens prepared with fresh water and cured in salt water. The concentration of the chloride ions near the surface of the reinforcement was increased with the increases of the charging time during the preparation for the corroded reinforcement. On the contrary, the chloride ions were likely bound in those specimens prepared with salt water and cured by saturated lime water. The concentration of the chloride ions near the surface of the reinforcement was higher than those near the outer surface. However, such influencing effects were not clear in the long term, possibly due to the hydration. The results of this study show that the reinforcement corrosion have influences on the diffusion of the chloride ions and such effect should be considered during the refinement of the traditional chloride ion diffusion models.
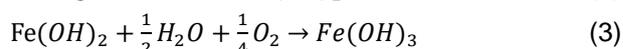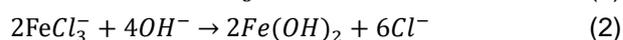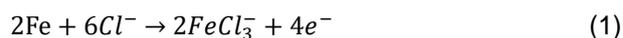
Keywords: reinforcement corrosion, chloride ion diffusion, open-circuit potential, linear polarization

1.0 INTRODUCTION

The durability of the coastal reinforced concrete structure is always an issue. Since the chloride ion intrusion is the main cause responsible for the corrosion of steel, the long-term exposure to high humidity and high salinity environment easily lead to the corrosion and further lead to the deterioration of reinforced concrete. In addition, the structures near the coastal areas may use locally produced aggregates, which generally have a high chloride content if they are not well pre-processed. In addition, local water sources containing high chlorides are possibly used for the mixing or curing purposes. Therefore, the reinforced structure may contain a large amount of chloride ions, leading to severe corrosion of steel bars and shortened service life. Therefore, to investigate the corrosion behavior of reinforcing bars and evaluate the performance degradation of the structural components, it is necessary to understand the movements of the chloride ions in concrete.

Corrosion of steel is an electrochemical reaction, and the corrosion begins only when the anode, cathode, conductive paths, current, and electrolyte are present (Revie and Uhlig, 2008). Pore solution of concrete is rich in various kinds of ions and plays the role of the electrolyte. In the alkaline solution, a passive layer is formed at the surface of the reinforcement. However, when the chloride ions exist, the passive layered can be destroyed, and the reaction is as follows (Jones, 1996):

$$2Fe + 6Cl^- \rightarrow 2FeCl_3^- + 4e^- \qquad (1)$$

$$2FeCl_3^- + 4OH^- \rightarrow 2Fe(OH)_2 + 6Cl^- \qquad (2)$$

$$Fe(OH)_2 + \frac{1}{2}H_2O + \frac{1}{4}O_2 \rightarrow Fe(OH)_3 \qquad (3)$$

It is learned from the above equations that the chloride ions are released during the reaction and further react with the iron, resulting in the continuous release of iron to form the rust. The chloride ion acts as a catalyst to further accelerate the corrosion. However, the presence of chloride does not necessarily contribute to the corrosion of steel, and its critical concentration depends on the pH of the pore solution near the rebar (Mindess *et al.*, 2003). In other words, the higher the pH of the pore solution, the less susceptible the steel bar is to corrosion.

Chloride ions in concrete are present in three forms: chemical bonded, physically adsorbed, and free chlorides. The former two forms are generally referred to as the bonded chloride ion, and it is generally accepted that the free chloride ion has a greater impact on the corrosion of steel (Arya *et al.*, 1990; Song *et al.*, 2008). The free chloride ions not

only come from the salt-contaminated concrete but also the unbound chlorides of the ingredients of the concrete, such as the aggregates and mineral additives. They move freely through the pore solution. The study aims to measure the concentration of the free chloride ion and relate that with the reinforcement corrosion.

The diffusion of chloride ion in concrete is generally described by Fick's law (Crank, 1959):

$$J(x) = -D\frac{dC}{dx} \tag{4}$$

where J is the diffusion rate of the ion (mol/cm^2/day), D is the coefficient of the diffusion (cm^2/day), c is the ionic concentration (mol/cm^3), and x is the distance of the diffusion (cm).

The coefficient of diffusion in concrete is not a constant and it is influenced by the hydration time, water-cement ratio and other factors (Nielsen and Geiker, 2003). However, it always takes a long time to observe the diffusion of the chloride ion in nature. Therefore, charging the embedded with electricity is generally used to speed up the movement of the chloride ions to facilitate the observation in the short term (ASTM, 2007(a)). However, the charging accelerates the corrosion of the reinforcement at the same time. Whether the corrosion affects the movement of chloride ions is not yet discussed.

To discuss the relationship between the corrosion of the reinforcements and the movement of chloride ions, the steel bars were firstly electrically charged to produce different degrees of corrosion. Then, the mortar specimens were prepared by mixing and curing with fresh or salt water. The content of the chloride ion in the specimen was measured, and then the corrosion of the embedded reinforcement was measured using the potentiostatic galvanostat to obtain the corrosion potential (ASTM, 2015) and to calculate the corrosion current density and the rate (Yang, 2008).

2.0   MATERIALS AND METHODS

2.1   Experimental Parameters

This study explores the relationship between the reinforcement corrosion and the migration of the chloride ion inside the reinforced mortar. The major experimental parameters are the duration of charging of the reinforcements, curing solution, and curing time, as summarized in Table 1. The reinforcements were pre-charged ranging from 3 to 24 hours before they were embedded in the mortar, so the corrosion was increased with the time. The specimens were cured either by fresh water or salt water (3.5% NaCl solution) to simulate the exposure of the reinforced concrete in the field. The ones prepared with the fresh-water mixing and curing in salt water (FMSC)

were used to simulate the reinforced concrete subjected to chloride ion intrusion, such as the seashore structure immersed in seawater. The chloride ion diffuses from the outside to the internal portion of the specimen. Those prepared with salt-water mixing and curing in salt-water (SMLC) were used to simulate the reinforced concrete containing salt-contaminated aggregates, such as the sea sands or those subjected to desalination.

Table 1. Experimental parameters and mix designations

Mixing water	Curing conditions	
	Saturated lime water	3.5% NaCl solution
Fresh water	–	FMSC
3.5% NaCl solution	SMLC	–

2.2   Sample Preparation

The cylindrical mortar specimens of φ10 mm×20 mm were prepared in reference to ASTM C192 (ASTM, 2007(b)). The mix design of the mortar is shown in Table 2. The #5 deformed bars were pre-charged before they were embedded in the mortar. The demolding was carried out one day after the casting, and the specimens were sealed at the top and the end by epoxy to limit the direction of the chloride ion permeation, as shown in Fig. 1. Specimens were cured either in the saturated lime water or salt water. The reinforcement corrosion measurements were conducted at the desired ages. After that, to determine the distribution of the chloride ions, the specimens were oven-dried, and the embedded reinforcements were taken out. The mortar was then sliced into three portions, each of which had 15 mm in thickness, as shown in Fig. 2. The sliced mortar was ground, powdered, and passed #200 sieve.

Table 2. Mix design of the mortar specimen

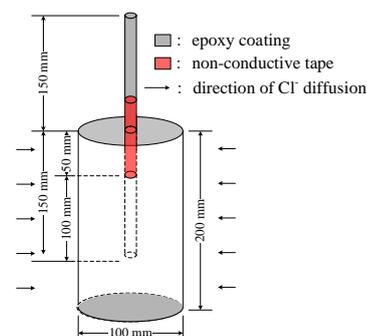| Materials	Weight (kg/m^3)
Cement (Portland Type I)	358
Water	215
Fine aggregates (surface-saturated dry)	1700

Fig. 1. Cylindrical mortar specimens with an embedded reinforcement
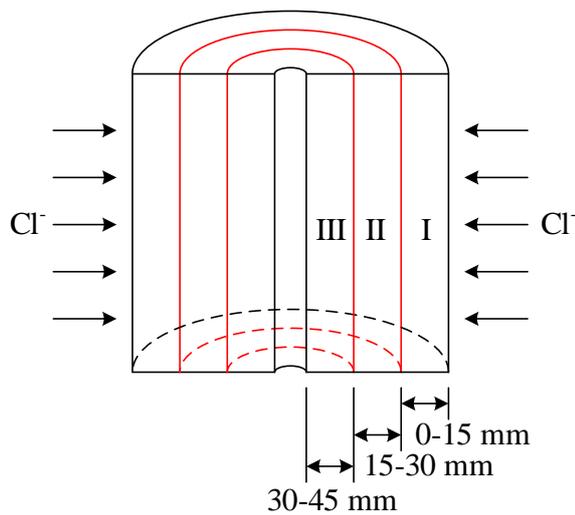
Fig. 2. Sliced portions of the reinforced mortar (I: the outermost portion, II: the middle portion, and III: the innermost portion)

2.3   Test Methods

This study involves the determination of the chloride ion concentrations and the reinforcement corrosion measurements. The concentration of the free chloride in the sliced portions of the specimen was measured in accordance with AASTHTO T260 (AASHTO 1997). On the other hand, the reinforcement corrosion was evaluated by the open-circuit potential (ASTM, 2015) and the corrosion rates measured by the linear polarization (Yang, 2008). The open-circuit potential was measured in accordance with ASTM C876, and it indicates the possibility of corrosion, as summarized in Table 3. However, its value is not correlated with the corrosion rate. To explore the influence of the chloride ion distribution on the corrosion rate of the reinforcement, a technique of the linear polarization was used.

In the linear polarization, a small potential of ±10 mV was applied during the measurement so that the polarization resistance (R_p) and the corrosion rate could be calculated using the Stern-Geary equation:

$$i_{corr} = \frac{B}{R_p} \qquad (5)$$

where i_{corr} is the corrosion rate (μA/cm^2), R_p is the polarization resistance ($\Omega\cdot$cm^2), and B is the Stern-Geary constant, taken as 0.0214 (mV)

Table 3. Probability of reinforcing steel corrosion (ASTM, 2015)

Half-cell potential		Probability of corrosion
CSE (mV)	SCE (mV)	
> -200	> -276	<10%
-200 − -350	-276 − -426	Uncertain
< -350	< -426	>90%

3.0   RESULTS AND DISCUSSION

3.1   Chloride Ion Distribution

<u>Fresh-Water Mixing and Salt-Water Curing (FMSC)</u>
Results are shown in Fig 3. Since the specimen was subjected to the salt water, its outer sliced portion had a higher concentration of the chloride ion. As the immersing time was increased, more chloride ion intruded, so the concentrations at both the outer and middle portion were increased. However, at the age of 7 days (Fig.3(b)), the innermost portion had a chloride ion concentration some greater than the middle. Moreover, such increases were associated with the increase of the charging time, suggesting that the chloride ion distribution was related to the reinforcement corrosion at early ages. Such phenomenon was not reported in the literature. It is likely that the locally concentrated ferrous ion (Fe^{2+}) and consumption of hydroxyl ion (OH^-) near the reinforcement attracted the chloride ion.
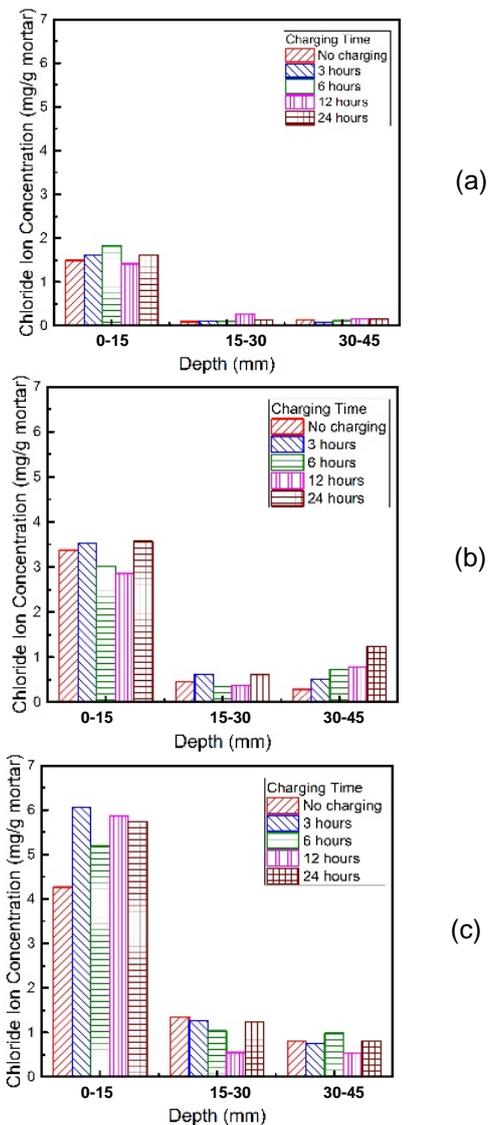

Fig. 3. Distribution of chloride ion in specimens FMSC with pre-charged reinforcements at ages of (a) 1 day, (b) 7 days, or (c) 28 days

At the age of 28 days (Fig.3(c)), the outermost portion had the highest concentration of chloride ion, followed by the middle and the innermost portion. However, the effect of the reinforcement corrosion on the chloride ion distribution was not clear anymore. It is likely that the hydration restricted the movement of the chloride ion. Moreover, in specimens with charging time of 12 or 24 hours, the free chloride ion concentration was even lower than those at the age of 7 days. It is likely that some chloride ions were incorporated in the hydrates, e.g., the formation of Friedel's salt.

Salt-Water Mixing and Saturated Lime-Water Curing (SMLC)
Results are shown in Fig 4. At the age of 1 day (Fig.4(a)), in general, the outmost portion had higher chloride ion concentrations than other portions. Since the specimens were cured in lime-water, the chloride ions tended to leach out. The distribution of the chloride ion appeared to be influenced by the pre-

charging time of the reinforcement. The specimen with reinforcement with the pre-charging time of 24 hours had smallest variations in the chloride ion concentration. Also, at the innermost portion, the pre-charged specimens at age of 1 day had high chloride ion concentrations (Fig. 4(a)), suggesting that the leaching of the chloride ions were inhibited. Again, it is likely that the reinforcement corrosion induced the attraction of the chloride ions.

At ages of 7 (Fig. 4(b)), such relationship between the chloride ion distribution and the charging time of the reinforcement was not clear. At the age of 28 days (Fig. 4(c)), the middle portion generally had higher chloride ion concentrations than others. It is supposed that the hydration restricts the movements of the chloride ions so that the chloride ions did not constantly leach out. The outer portion subjected to the lime water possibly had higher degree of the hydration than the inner one, so the free chloride ions were reduced. However, at the innermost portion, the chloride ion concentrations were reduced in those specimens with pre-charged reinforcements. The mechanism was not clear. The corroded reinforcement could lead to a locally porous region such that the chloride ions were easy to migrate.

In summary, the results of the study show that the reinforcement corrosion likely influences the movement of the chloride ions, especially at early ages. The mechanism is not clear and needs further investigations. However, in the long term, the hydration plays an important role. The movements of the chloride ions were restricted.

3.2 Open-Circuit Potential

Fresh-Water Mixing and Salt-Water Curing (FMSC)
Results are shown in Fig. 5(a). At curing time of 1 day, those reinforcements pre-charged for 12 hours and more showed lower potential than the plain, indicating the charging-induced accelerated corrosion. However, with charging time of 3 and 6 hours, the reinforcements had high potentials, even higher than that without charging. Such increase in potential was likely due to the passivation formed in the alkaline environment in the mortar. Slightly accelerated corrosion could induce oxides at the surface of the reinforcements. At curing of time of 7 and 28 days, all pre-charged reinforcements showed low potentials, indicating the high possibilities of corrosion. It should be noted that, firstly, those reinforcements pre-charged for 12 and 24 hours in specimens at curing time of 28 days had drops in potential more than those pre-charged for 3 and 6 hours, suggesting that the attracted chloride ions might impose the delayed corrosion. Secondly, all the pre-charged reinforcements had much lower potential than those without pre-charging, implying that the pre-charged reinforcements were vulnerable to the salt attack.
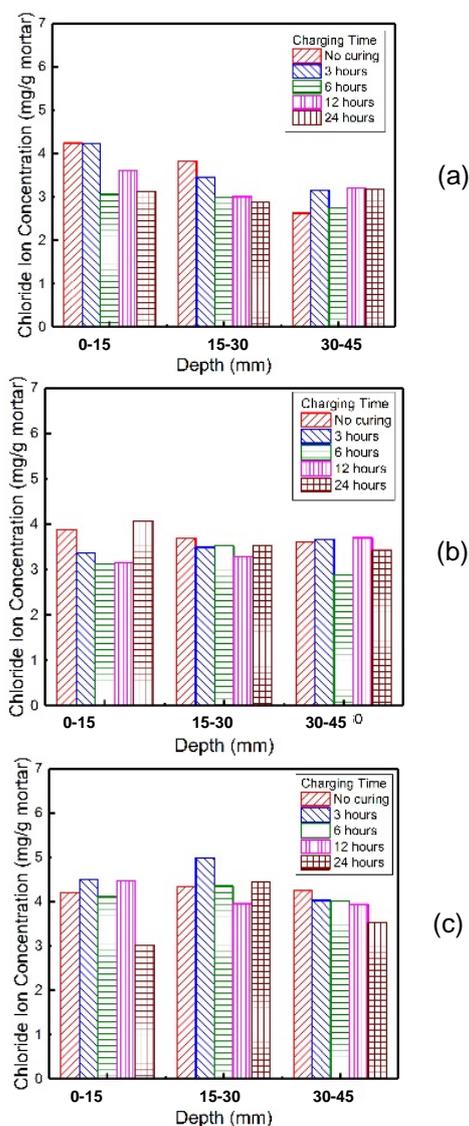

Fig. 4. Distribution of chloride ion in specimens (SMLC) with pre-charged reinforcements at ages of (a) 1 day, (b) 7 days, or (c) 28 days

Salt-Water Mixing and Saturated Lime-Water Curing (SMLC)
Results are shown in Fig. 5(b). At curing age of 1 day, the reinforcement without charging has a low potential because the specimen was prepared by salt water and the chloride ion concentration was high. However, the reinforcement with the pre-charging time of 3 hours had a high potential. It is likely the iron oxides provided a passive protection. As the curing ages are increased, all the reinforcements showed high probabilities of corrosion. In general, at curing age of 7 days, the corrosion potentials were lower than that of FMSC, again showing the effect of high chloride ion concentration.
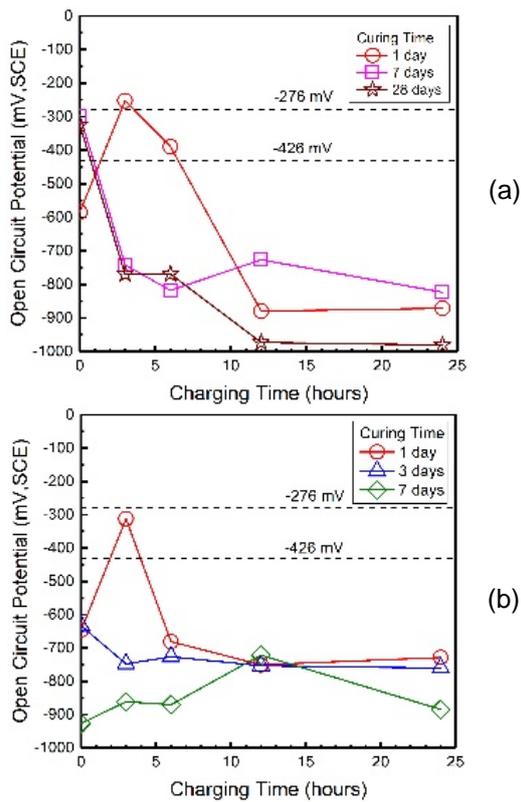

(a)

(b)

Fig. 5. Relationship between the open-circuit potential and the charging time of the reinforcement in (a)FMSC, or (b)SMLC at different curing time

In summary, the results of this study have shown that the pre-charging induced corrosion. A slight pre-charging could induce passivation at the early age.

3.3 Corrosion Rates

Fresh-Water Mixing and Salt-Water Curing (FMSC)
The corrosion rate of the reinforcement was related to the chloride ion concentration at the innermost portion. Results are shown in Fig. 6(a). In general, the overall relationship between the corrosion rate and the chloride ion concentration was not clear. However, at the age of 1 day, the corrosion rate was proportional to the chloride ion concentration, suggesting that high chloride ion concentrations induced high corrosion. At the later time, such relationship was not clear probably because the linear

polarization did not separate the resistance of mortar, so the changes in the mortar properties by hydration affected the corrosion measurements.

Salt-Water Mixing and Saturated Lime-Water Curing (SMLC)
Results are shown in Fig. 6(b). The overall relationship between the corrosion rate and the chloride ion concentration was not clear. Again, the linear relationship likely occurred at the age of 1 day. During the early age, the mortar was not well hydrated, and the resistance of the mortar was low, so the corrosion measurement was less influenced.

When compared with FMSC specimens, the SMLC specimens had corrosion rates within the same order even though the chloride ion concentrations were high. Such results suggest that the high corrosion rates were attributed to the pre-charging rather the chloride ions. The corroded reinforcements further altered the distribution of chloride ions.
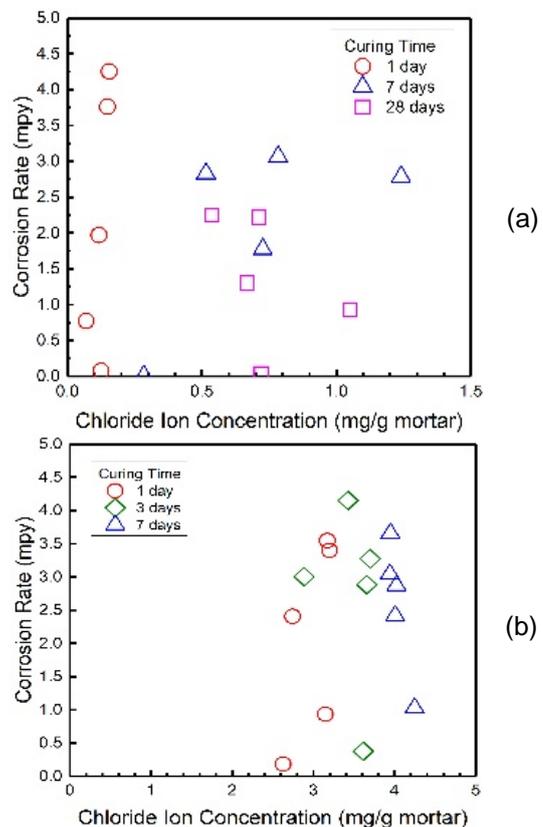

(a)

(b)

Fig. 6. Relationship between the corrosion rate and the chloride ion concentration in specimens of (a)FMSC, or (b)SMLC with different curing time

In summary, by linear polarization, the corrosion rate of the reinforcement was not well correlated with the chloride content. However, at early hydration time, the corrosion rate was increased with the chloride ion concentration, suggesting that the corrosion could attract the chloride ions, agree with the results by chloride ion distributions. On the other hand, the technique of the linear polarization has its limitations. The actual corrosion rates of the reinforcements are

larger than the ones shown in the results previously because the measured polarization resistance is the sum of the resistances of the mortar cover and the reinforcement. The property of the hydrating mortar can be an influencing factor, but the linear polarization cannot the tell the changes. It is likely that such drawback of the technique leads to the uncertainty in the measured corrosion rates of the reinforcement at the late hydration time.

4.0 CONCLUSIONS

This study explores the relationship between the reinforcement corrosion and the chloride ion movements in mortar specimens prepared with different ways of mixing and curing. Results showed that reinforcement corrosion altered the distribution of the free chloride ions. At early hydration time, the reinforcement corrosion likely attracted the chloride ions, thereby inducing higher chloride ion concentrations in the vicinity of the reinforcements. As the hydration time was increased, such relationship was not clear probably because the hydration restricted the movements of the chloride ions and the linear polarization overlook the changes of the mortar properties in the long term. Therefore, to explore the diffusion behaviors of the chloride ion in reinforced concrete, it is necessary to consider not only the microstructural changes due to the hydration but also the corrosion of the reinforcement, which could accelerate the chloride ion intrusion locally.

Acknowledgement

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