

INFLUENCE OF MORTAR MIXED WITH ION EXCHANGE RESIN ON RESTRAINT OF CHLORIDE ION IN PC BRIDGES

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Abstract: Corrosion of prestressing tendons is the governing factor of deterioration in prestressed concrete (PC) bridges, which affects structural performance in terms of serviceability and load-carrying capacity. In Japan, the major cause of deterioration in PC bridges is corrosion due to chloride attack from airborne salt or deicing chemicals. The objective of this study is to develop highly durable mortar using ion exchange resin as an admixture mix with different cement types. In here, quantitatively evaluates the diffusive behavior of chloride ions into the mortar mixed with admixture and discusses about its influence to reduce free mobile chloride ions. A number of immersion tests were conducted using mortar specimens made with different cement types and admixture with different ratios. Then, acid soluble, free and bound chlorides were measured at the different time periods. The test results show the significant enhancement of chloride binding in mortar with ion-exchange resin.

Keywords: Prestressed concrete, Chloride induced corrosion, Ion exchange resin admixture

1. INTRODUCTION

Prestressed concrete (PC) technology is widely being used all over the world in construction of wide range of structures, particularly bridge structures. In Japan, the application of prestressed concrete was first introduced in the 1950s, and since then, the construction of PC bridges has grown considerably. The increased interest in the construction of PC bridges can be attributed to the fact that the initial and life cycle cost of PC bridges, including repair and maintenance, are much lower than those of steel bridges. (Mutsuyoshi and Hai., 2010). Moreover, comparing to the reinforced concrete (RC) bridges, PC bridges are more economically competitive and aesthetically superior due to the employment of high strength materials. PC structures properly designed and constructed generally have been considered highly durable because the prestressing tendons could be protected from corrosion by filling the duct with cement grout. In recent years, however, deterioration problems have been discovered in some existing PC bridges, raising serious concerns about the long term durability of them. As a consequence, the long term durability has become a particular concern and should seriously be considered in the design and construction of PC bridges apart from the view point of structural safety, aesthetic values and cost.

The major cause of deterioration in PC bridges is the corrosion of prestressing tendons, which affects structural performance in terms of serviceability and load-carrying capacity. Collapses of three internal post-tensioned bridges are reported without warning in the UK and Belgium (Schokker et al., 2001). The main reason for these collapses was deterioration of the prestressing tendons. In Japan, the major cause of deterioration in PC bridges is corrosion due to chloride attack from airborne salt from the sea, or the use of deicing chemicals. Many researchers have studied corrosion of RC structures under chloride attack (Yoon et al., 2000) and its mechanism is being clarified. In contrast, few studies have investigated the influence of chloride ions on the corrosion of PC bridges. The free mobile chloride ion inside the sheath plays a dominant role in corrosion of prestressing tendons.

In Japan, even though a number of innovative technologies have been developed to increase the structural performance and the long term durability of PC bridges, the elimination of free chloride ion inside the sheath has not yet been clarified. Nowadays, study in the purpose to control penetration is accomplished in Japan, radical results of research that we approached from construction material side doesn't appear so far. Thus, we focused our attention to ion exchange resin as an admixture which has ability to absorb and bind free chloride ions, once induced into the structures, and the objective of this study is to present the influence of admixture to restraint chloride ions in PC bridges.

2. EXPERIMENTAL PROGRAM

2.1 Materials

(1) Ion exchange resin admixture

One of typical commercially available anion exchange resin, type 1 strongly basic, clear gel, has been examined. It has a cross linked polystyrene structure that is designed to give an optimum balance of capacity and regeneration efficiency. The total exchange capacity of resin is greater than 1.25eq/L and the moisture holding

capacity is 49 to 60%. The resin is prepared as spherical beads of 0.50mm in diameter and used in powder form after regenerated it into the hydroxyl form. The admixture is insoluble substance containing loosely held ions which are able to be exchanged with other ions in solution which comes and contact with them. These exchanges take place without any physical alteration to the ion exchange. Thus, once chlorides induced to the fresh concrete, resin absorb and bind the chloride ions and liberate hydroxyl ions into the pore solution. This action results in both reduction of free chlorides and enhances the alkalinity of the pore solution by passivating the steel reinforcement.

(2) Cement types

The two types of cements were used in this study. They are, high early strength portland cement which contains 9% tricalcium aluminate (C_3A) and 8% tetra calcium aluminoferrite (C_4AF) by mass and ground granulated blast furnace slag cement which contains 9% alumina (Al_2O_3) by mass.

2.2 Experiment Method

Twenty four mortar specimens (10cm x 10cm x 10cm) were altogether casted and exposed to chloride penetration. To enable realistic comparisons, all cubes were made with the same total cementitious content of 586 kg/m^3 and the same water/cement ratio of 0.50. Specimens were made using high early strength portland cement (HPC) and ground granulated blast furnace slag cement (BFS) mixed with ion-exchange resin admixture with different mix ratios as shown in Table 1. After casting, the specimens were covered by polyethylene sheets for 24 hours. The HPC and BFC specimens were then demolded and cured by covering wet clothes continuously for 14 days and 28 days respectively. Five sides of the cubes were then coated with epoxy paint to leave the other side for one-dimensional chloride diffusion.

Immediately after curing, all the cubes were exposed to chloride penetration regime, consisting of 1 day of ponding with an aqueous solution of 10% sodium chloride (NaCl) followed by 6 days of drying with constant temperature and humidity of 20°C and 60% RH respectively. All the specimens were exposed to a total of 12 cycles in steps of 28 days, 56 days and 84 days. After the completion of the exposure regime, test specimens were sliced into the layers as 0 to 10 mm, 13 to 23 mm, 26 to 36 mm & 39 to 49 mm and then passed through a jaw crusher separately. The powdered samples were then passed through a sieve having an aperture size of 150 μm , and the powders thus obtained were used for chloride analyses.

Table 1- Details of mix ingredients in test specimens (kg/m^3)

Specimen Type	Cement	Water	Sand	Admixture
S1:HPC & S5:BFS	586	293	1259	0
S2:HPC/1% admixture & S6:BFS/1% admixture	586	293	1248	11
S3:HPC/2% admixture & S7:BFS/2% admixture	586	293	1238	21
S4:HPC/2% admixture & S8:BFS/2% admixture	586	293	1227	32

2.3 Calculate Diffusion Coefficient

The diffusion coefficient for the chloride ions penetrating through cement mortar specimens is estimated by assuming the chloride diffusion to follow the steady state process. In general, Fick's 2nd law is a good approximation for the calculation of the chloride penetration into concrete (Suryavanshi et al., 2002).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

By assuming $C(x, 0) = 0$, $C(0, t) = C_0$ and constant diffusion coefficient (D), the solution of Eq.(1) is,

$$C(x,t) = C_0 \left[1 - \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right] \quad (2)$$

Where, C_0 is the chloride concentration at the surface (kg/m^3), $C(x, t)$ is the measured chloride concentration at x (cm) depth in t (years) time (kg/m^3), D is the effective diffusion coefficient ($cm^2/year$) and erf is the error function.

3. TEST RESULTS AND DISCUSSION

Table 2 quantifies the acid soluble chlorides present in all the specimens at different depth intervals in different exposed periods. By considering the results, the acid soluble chlorides at the surface layer (0 to 10 mm) were considerably high comparing with other depth intervals for all the specimens. In general, it is due to its close proximity to the ponding surface, and there is also the possibility of salt precipitation in the surface defects such as

blow holes, voids and cracks during the drying periods. Therefore, the results of remaining depth intervals were only considered except surface depth for the analysis in all specimens.

Table 2 – Acid soluble chlorides present at various depths in all tested specimens in three time periods.

Spec. Type	28 days expose period				56 days expose period				84 days expose period			
	0-10mm	13-23mm	26-36mm	39-49mm	0-10mm	13-23mm	26-36mm	39-49mm	0-10mm	13-23mm	26-36mm	39-49mm
S1	5.0945	0.0501	0.0826	0.0594	11.005	0.0659	0.0113	0.0888	9.8869	0.2336	0.1148	0.0546
S2	7.0641	0.2253	0.1944	0.2223	10.364	0.2752	0.2565	0.2934	14.609	0.3957	0.2752	0.2700
S3	6.4453	0.6050	0.4641	0.4507	10.629	0.4910	0.3970	0.4182	14.599	0.5300	0.4810	0.4524
S4	7.5923	0.5859	0.6076	0.4871	8.9340	0.6240	0.6045	0.6154	16.170	0.8554	0.7649	0.8017
S5	4.6533	0.0923	0.0772	0.0763	6.7622	0.1655	0.1134	0.1746	7.8702	0.1565	0.0927	0.0871
S6	4.5688	0.3082	0.2806	0.2449	8.4780	0.4393	0.3449	0.2815	9.7222	0.4397	0.3815	0.3276
S7	6.4674	0.6454	0.5695	0.4302	9.9580	0.5600	0.4859	0.4738	10.802	0.8256	0.6354	0.6079
S8	5.4620	0.6833	0.6346	0.6212	8.7168	0.7510	0.7424	0.6777	12.347	1.0282	0.7639	0.8855

Fig. 1 shows the acid-soluble chloride profiles for the HPC and BFS mortar specimens tested after 84 days respectively.

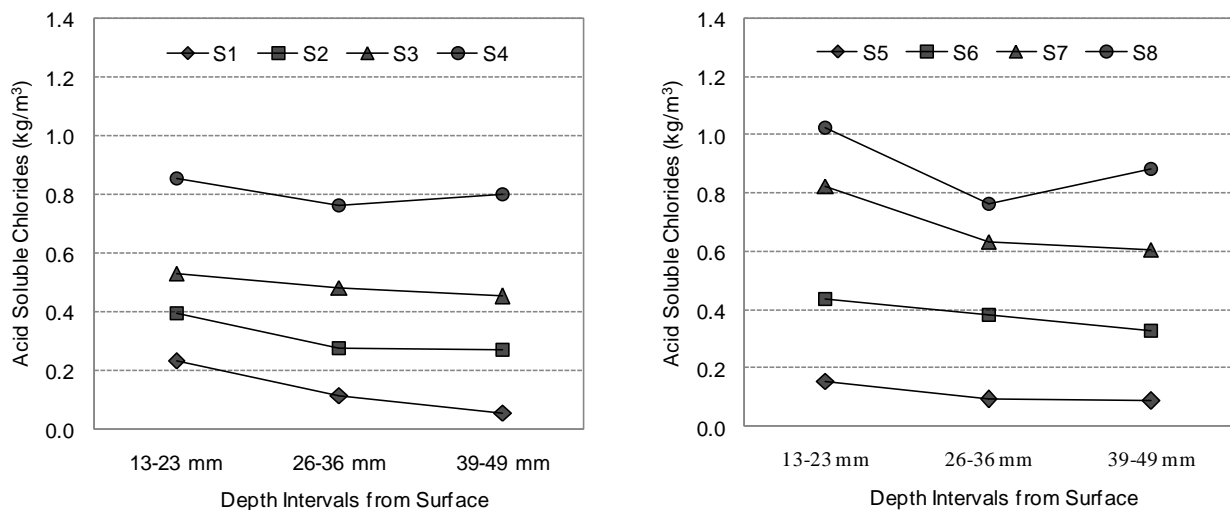


Fig.1 Acid-soluble chloride profile at 84 days in HPC and BFS specimen

The test results show that the amount of chlorides present at different depth intervals consistently decreased with increasing distance from the top exposed surface of the specimens. Moreover, the acid soluble chlorides present at any given depth intervals significantly increased with increasing of admixture percentage in mortar. For example, specimen S4, cast with HPC and 3% admixture shows the largest amount of chlorides at all depth intervals compared with other specimens S1, S2 and S3. On the other hand, control specimen S1, made with HPC mortar only without mixing admixture, shows the least amount of chlorides compared with other specimens S2, S3 and S4 at all depth intervals investigated. The chlorides content at all the depth intervals investigated for specimens S2 and S3 was extent between specimens S1 and S4, as we expected. Thus, the amount of acid soluble chlorides and their depth of penetration are a direct function of the absorption and binding capacity of ion exchange resin admixture in the mortar mixture. Further, apart from that relationship, the BFS specimens S5, S6, S7 and S8, show the increment of acid soluble chlorides at all the depth levels compared to the HPC Specimens.

When chlorides accumulate within the surface layer of concrete, a concentration gradient of chloride ions is established within the concrete cover with the result that chloride ions migrate towards the deep depths. Moreover, the specimens also subjected to cyclic wetting and drying process and thus, the chloride ions can also be absorbed by capillary or move in and out of concrete by convection. However, the chloride ingress by absorption only takes place within the top 5 to 10 mm layer (Nanukuttan et al., 2008). Thus, diffusion is the dominant transport mechanism responsible for chloride movement to greater depths within the cover zone. Fig. 2 shows the estimated diffusion coefficients in different time intervals for the HPC and BFS mortar specimens respectively. The least square fit method was used to calculate the diffusion coefficients (D) for the tested specimens. Diffusion coefficient represents the rate of chloride penetration into the mortar specimen.

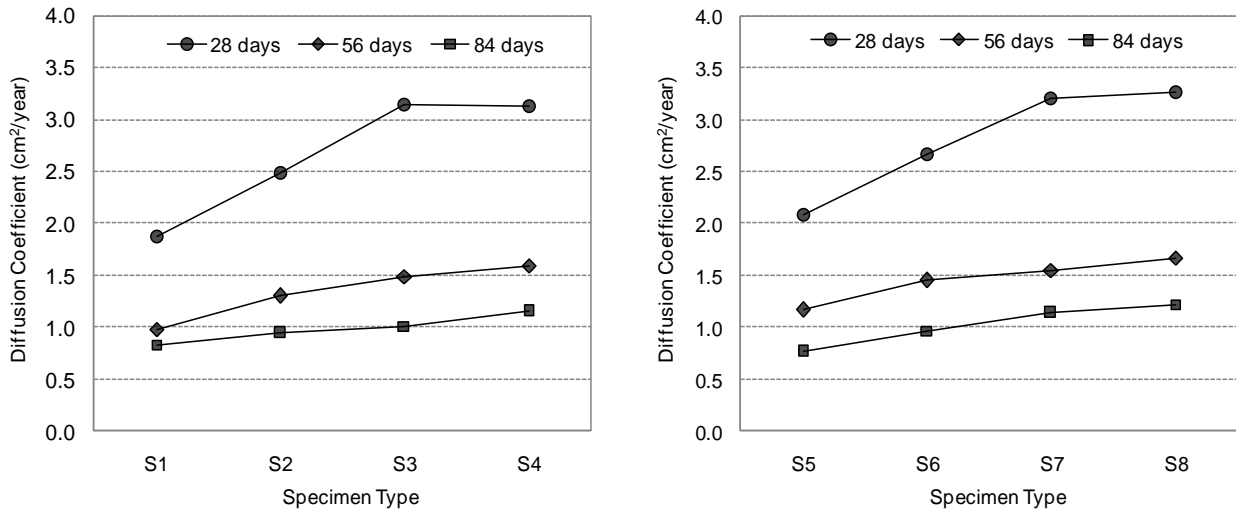


Fig. 2 Chloride diffusion rate in HPC and BFS specimens

Initially, the estimated diffusion coefficients in the tested specimens show the significant increment with increase of mix percentage of admixture (for 28 days exposed period). The penetration of chloride ions towards the specimen was increased at the beginning due to high concentration gradient between NaCl solution and mortar specimens. At the beginning, there wasn't any back ground chloride concentration in all specimens. Once chloride induced into the mortar specimens, the ion-exchange resin effectively absorbed and bound the chlorides. That phenomenon was allowed to penetrate more chlorides into the specimens consistently, by increasing concentration gradient between inside and outside of the specimen comparing with the control specimen. However, the comparison of results with time, considerable reduction was observed in both types of specimens at the end of 84 days exposed period. Further, diffusion coefficient of control specimens (S1 and S5) was almost similar with the other specimens. Therefore, while chloride penetration rate was increased in beginning with increment of mixed admixture percentage, the penetration rate was reduced with time and approximately similar in all specimens. Thus, the penetration of chlorides into the greater depths significantly reduced and the accumulation of free chlorides near the reinforcement layer depth also reduced.

Fig. 3 represents the significant result of chloride binding by admixture. While the chloride diffusion rate of all the tested specimens was identical with time, the affinity of chloride absorption and binding were noticeably increased with exposed period. Hence, the chloride binding of admixture was increased while chloride penetration was reduced, with increasing of exposed period. The test results further show that the chloride absorption and binding ability were dominant in BFS specimens comparing with HPC specimens with increase of time.

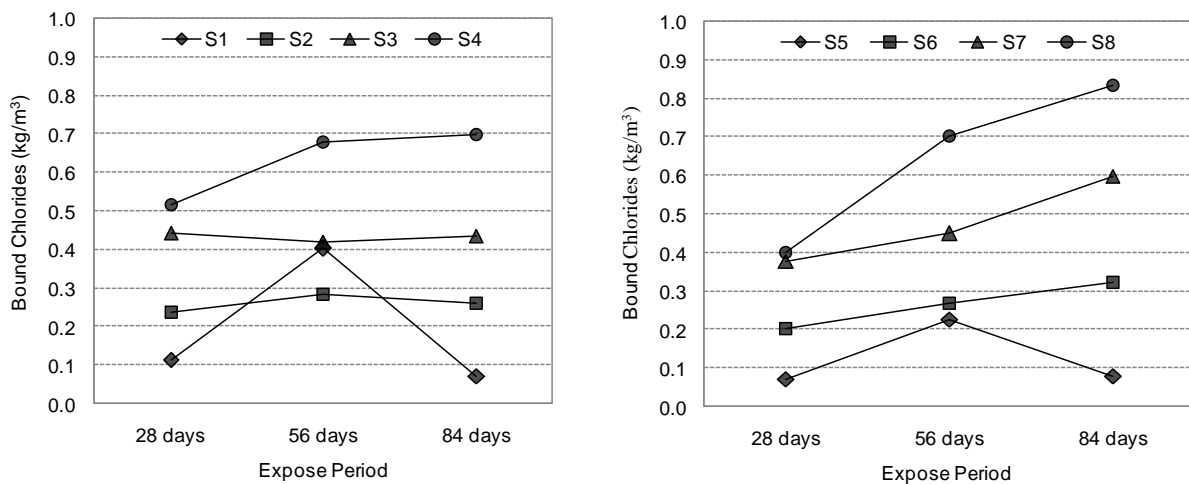


Fig.3 Bound chloride profile at 39-49 mm depth in HPC and BFS specimens

Fig. 4 shows the free chloride and bound chloride profiles at 39 to 49 mm depth interval for the all HPC and BFS mortar specimens mixed with different ratios of admixture in 84 days respectively. In general, 50 mm concrete cover is used for the RC structures built in marine environments. Thus, the bound and free chlorides were taken at this depth interval to simulate the actual condition near the reinforcing steel layer.

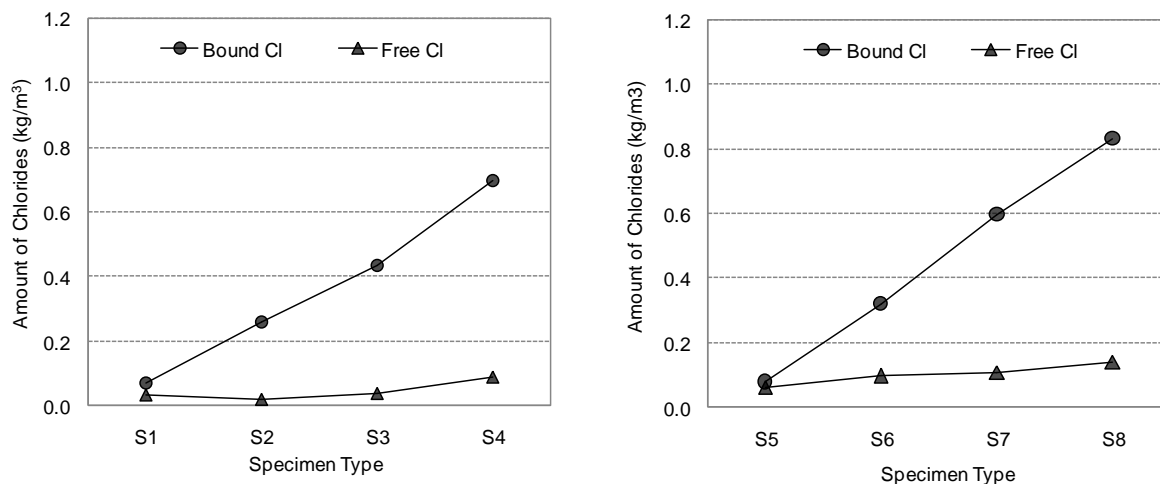


Fig.4 Chloride profiles in 39-49 mm depth at 84 days in HPC and BFS specimens

The test results show that the amount of bound chlorides at the 39 to 49mm depth in all specimens were significantly increased with increasing mixed amount of ion exchange resin admixture, compared with control specimens. Further, absorption and binding of chlorides in BFS mortar specimens were dominant than HPC specimens. Free chlorides were slightly increased with increase of admixture percentage in all specimens. However, the increment of free chlorides in pore solution was infinitesimal, comparing with penetrated chlorides into the specimen.

The induced chloride ions into the mortar can also be bound to the cement hydrates and their surfaces either chemically or physically, except the newly mixed admixture. Chlorides react with the unhydrated aluminates phases to form new compounds such as calcium monochloroaluminates (or Friedel's salt), calcium trichloroaluminates, and chloroferrite hydrates (Delagrave et al., 1997). Recent studies have also clearly established that chlorides can chemically and physically interact with the calcium silicate hydrates (C-S-H) (Beaudoin et al., 1990). Thus, the C_3A and C_4AF of HPC cement and alumina content of the BFS cement also participated to the chloride binding, once induced to the mortar. Moreover, the chloride binding capacity and reinforcement corrosion initiation time can be increased by 2.43 and 2.45 folds, respectively, in accordance with increase of C_3A content from 2% to 14% (Hussain et al., 1995).

However, the test results show the significant chloride binding at ion exchange resin mixed mortar specimens contrast with cement compositions such as unhydrated aluminates phases and C-S-H gel. It can be clearly understood comparing with control specimens, S1 and S5. Thus, the newly mixed ion exchange resin admixture is increased the chloride binding instead of those phases in cement types. As a result of that, the free chloride ions in the pore solution also reduced effectively.

Arya et al. (1990) has shown that partial substitution of cement with ground granulated blast furnace slag increases the chloride binding in the case of internal and external chlorides. Dhir et al. (1997) suggested that high binding capacity of cement-slag phase may be due to the high alumina content in slag, resulting in the formation of more Friedel's salt. Arya et al. (1990) also suggested that the increase in adsorbed chlorides is responsible for the higher level of binding. Thus, the acid soluble and bound chlorides were considerably increased in BFS specimens contrasting with HPC specimens due to higher binding capacity of blast furnace slag cement.

4. CONCLUSIONS

The major conclusions derived from this study are given as follows:

- (1) The amount of acid-soluble chloride and the depth of penetration into the concrete decreases with increasing distance from the top exposed surface of the specimens. The acid soluble chlorides present at any given depths significantly increased with increasing of admixture percentage in mortar.
- (2) The amount of acid soluble chlorides and their depth of penetration are a direct function of the absorption and binding capacity of ion exchange resin admixture in the mortar mixture.
- (3) Initially, the chloride penetration rate was increased with increase of mixed percentage in admixture. However, the penetration rate was noticeably reduced with time and later, almost identical with control specimens.
- (4) While the chloride diffusion rate was similar in all specimens, the affinity of chloride absorption and binding were noticeably increased with expose period. Hence, the admixture effectively bound chlorides with time.
- (5) Free chlorides were slightly increased with increase of admixture percentage in all specimens. However, the increment of free chlorides in pore solution was infinitesimal, comparing with penetrated chlorides (acid soluble chlorides) into the specimen.

- (6) The newly mixed ion exchange resin admixture increased the chloride binding in mortar instead of other binding agents (unhydrated aluminates phases and C-S-H gel) in cement types.
- (7) Blast furnace slag cement has higher binding capacity due to the high alumina content in slag, resulting in the formation of more Friedel's salt. Thus, the acid soluble and bound chlorides were considerably increased in BFS specimens contrasting with HPC specimens.

ACKNOWLEDGEMENT

The authors would like to acknowledge Mr. Nito Nobukazu & Mr. Uehira Kenji in DC Co. Ltd. and Mr. Yamanaka Kouji & Miss. Tomomi Nanakashi in Organo Corporation for their advices and supply of materials for this research study.

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