Influence of ion exchange resin in chloride binding for RC structures exposed to marine environment

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ABSTRACT: Chloride-induced corrosion is one of the major deterioration phenomena of Reinforced Concrete (RC) structures worldwide, especially in marine atmosphere. When chloride ions ingress into RC structures by diffusion process, they severely damage the structures in the form of cracking, spalling or delamination which reduce the life span of existing RC structures and warrant untimely expensive repair as well. In coastal areas, RC structures deteriorate seriously only due to chloride attack. In recent years, study in purpose to control penetration of chloride inside concrete structures got emphasis and researchers are approaching with innovative ideas but radical results from construction material side not appeared yet. Thus, this study focused on using ion exchange resin in concrete structures which has wonderful ability to absorb and bind chloride ions. The objective of this study is to assess the influence of Ion Exchange Resin (IER) for chloride absorption and binding when used in concrete structures exposed to marine atmosphere. Now a day, there are some commercially available anion exchange resins which have excellent ion exchange and binding capacity. This paper will examine, how ion exchange resin combining with cement mortar, could be a potentially effective option to bind chloride and reduce chloride induced corrosion in RC structures. A number of immersion tests were conducted using mortar specimens of different types of cement. The mortar specimens of 10cmX10cmX8cm size were prepared which contained different percentage of resin by volume. The prepared specimens were immersed into 10% sodium chloride (NaCl) solution for one day and then exposed in drying condition for 6 days. This cycle was repeated for a specific time regime. Then chloride contents at different depths in all specimens were measured for each time regime. The test results signify the potential enhancement of chloride absorption and binding into the concrete by the resin admixture. This potential uses of resin into cement matrix could be a good option for real RC structures for mitigating the chloride induced corrosion

1 INTRODUCTION

Concrete is the most versatile and widely used construction material all over the world but corrosion, especially chloride induced corrosion which may lead to reduction in strength, serviceability, and aesthetics of the RC structures is probably the most vital and common threat for material durability. As a result, durability of RC structures in chloride laden environment is of great interest to design engineers, infrastructure owners and researchers (Shi et al. 2012). In case of RC structures, with passing of time, chlorides from the environment penetrate into the structures and get accumulated, what we call the matured concrete structures. The accumulation and ingress of chloride ion corrode the reinforcement (Elsener 2002). Due to chloride induced corrosion, structures require immediate repair and untimely maintenance. If we could identify the phenomena of chloride ingress into the concrete structures and the chemistry how it accelerates the corrosion, then the development of countermeasure would be the effective solution in controlling the chloride attack. The repair of damaged RC structures can be done, using some ready-mixed mortars (Batis et al. 2003), prepared by using different kinds of additives, such as ion exchange resin, silica fume or fly ashes. These admixture substances should have good characteristics quality compatible with concrete and should not alter the properties of concrete as well. In the present study, a typically available commercial Ion (anion) Exchange Resin (IER) has been examined with two types of cement to justify and determine the chloride absorption and binding potentiality of IER. IER are polymers of spherical beads of 0.5 to 1.0 mm diameter and insoluble substances, containing loosely held ions which are able to be exchanged with other ions. These exchanges take place without any physical alteration to the ion exchange material. This results in the reduction of free chloride in the pore solution and increase the alkalinity of concrete structures which ultimately re-passivate the steel reinforcement. A number of immersion tests were conducted using small mortar specimens of High-Early Strength Portland Cement (HESPC) and Polymer Cement (PC) which contains 0%, 1%, 2% and 3 % IER by volume. The resin absorbs and binds chloride ions from the matured concrete structures and liberates hydroxyl ions into the pore solution and enhances the alkalinity. This paper will examine, how ion exchange resin combining with cement mortar, could be a potentially effective option to bind chloride and reduce chloride induced corrosion of RC structures.

2 METHODOLOGY OF STUDY

2.1 Materials and Mix Proportions

Immersion tests were conducted to examine the chloride absorption and binding capacity of IER. Two types of specimens were prepared both using HESPC and PC, one type for potentiometric titration analysis and the other one for Electron Probe Micro Analysis (EPMA), whose geometry and dimensions are shown in Figure1. A strongly basic & typical commercially available anion exchange resin has been used in this study. The total exchange capacity of resin is greater than 1.25eq/L (Cl- form) and the moisture holding capacity is 49 to 55% with 660 g/L-R apparent density. The physical properties and chemical compositions of HESPC and PC are listed in Table 1. The specimens and their mix proportions are listed in Table 2 & Table 3, where 0% IER mixed specimens were the control specimens and 1%, 2% & 3% IER mixed specimen were the test specimens.



(c) Main Specimen for EPMA (d) Sliced Specimen for EPMA (e) EPMA Analysis area Figure 1. Geometry and dimensions of specimens for titration analysis in (a), (b) & for EPMA in (c),(d), (e)

Table 1. Physical properties and chemical compositions of HESPC and PC

Cement Type	Density (g/cm3)	Chemical Composition (% by mass)									
HESPC	3.14	(Na ₂ O+K ₂ O) 1.624	SiO_2 20	Al ₂ O ₃ 5.01	Fe ₂ O ₃ 2.79	CaO 65.9	MgO 1.55	SO ₃ 3.12	NaCl 0.006		
PC	3.15	Latex fibre 12-23	(SiO ₂ +NaCl) 40-50		Al ₂ O ₃ 6.00	Hydraulic cement (OPC) 20-25			PC)		

Table 2.	Test	specimens	and	their	mix	proportions	for	HESPC	(kg/m^3))
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Specimen Type	IER (%)	W/ C Ratio	Water	Cement	Sand	Resin	Remarks
S1: IER (0%)	0	0.5	293	586	1259	0	Control Specimen
S2: IER (1%)	1	0.5	293	586	1248	12	Test Specimen
S3: IER (2%)	2	0.5	293	586	1238	23	Test Specimen
S4: IER (3%)	3	0.5	293	586	1227	35	Test Specimen

Table 3. Test specimens and their mix proportions for PC (kg/m³)

Specimen Type	IER (%)	W/ C Ratio	Water	Cement	Resin	Remarks
S1: IER (0%)	0	0.5	315	1750	0	Control Specimen
S2: IER (1%)	1	0.5	315	1724	12	Test Specimen
S3: IER (2%)	2	0.5	315	1698	23	Test Specimen
S4: IER (3%)	3	0.5	315	1673	35	Test Specimen

2.2 Exposure Conditions and Analysis of Test Specimens

After casting, each specimen cured by wrapping in wet cloth film to avoid leaching out of chloride ions from the cement matrix. This curing procedure was applied to the specimen for a period of 14 days. At the end of curing period, five sides of each specimen were sealed by epoxy paint (see Figure1 (a) & Figure1(c)) so that the chloride penetration can occur only in one-direction. Immediately after sealing, all cubes were immersed into chloride penetration regime, consisting of 1 day of ponding in 10% sodium chloride solution followed by 6 days of drying with constant temperature of 20°C and 60% RH. Specimens were exposed to the above mentioned penetration regime for a period of 28 days, 56 days and 84 days. For titration analysis, after each exposure regime, specimens were sliced into the layers from 0 to 10 mm, 13 to 23 mm, 26 to 36 mm & 39 to 49 mm as shown in Figure 1(b) and grounded separately for potentiometric titration analysis against AgNO3. For EPMA, specimens were sliced into layers and analyzed as shown in Figure 1(d) & Figure 1(e).

3 RESULTS AND DISCUSSIONS

3.1 Titration Analysis

The trend of chloride accumulation and absorption in HESPC and PC mortar specimens for different time periods were measured quantitatively by silver nitrate potentiometric titration method and presented in Figure 2.



Figure 2. Chloride profile in (a) 28 days: HESPC, (b) 56 days: HESPC, (c) 28 days: PC and (d) 56 days: PC

In general, the chlorides inside the concrete structures mainly participate in corrosion process and corrode the reinforcement. It was observed that, total chloride content increased with increment of IER (admixture) percentage in all specimens. Test specimen S4 which contained 3% IER (admixture) showed the largest amount of chloride absorption whereas the control specimens S1 showed the least amount of chloride absorption. Thus, it clearly represents that, there exists a direct relationship between admixture percentage and increment of chloride content. Generally, the summation of bound chloride and free chloride content equals to the total chloride, bound chloride and free chloride content for different time exposure for HESPC and PC was calculated. The results revealed that test specimen showed much better performance of chloride binding than control specimens and it increased with the passes of time. This phenomena

was also depicted in Figure 3 where chloride binding capacity, Cl_{bc} (= $\partial C_b/\partial C_{f,}$) (where C_b and C_f are respectively the bound and free chloride) changes when the ion concentration changes. From the graphical presentation it was clearly depicted that resin content has a direct influence in chloride binding when they are mixed with the mortar. Hence, this phenomenon was the indication that, if cement matrix contains resin, then with passes of time, more amount of penetrated chloride will be bound with the resin beads leaving less amount of available free chloride to corrode the reinforcement. In this chloride binding, newly mixed IER admixture



Figure 3. Chloride Binding Isotherm for (a) PC-S3: IER (2%) & (b) HESPC-S4: IER (3%)

plays a dominant role. However, these results confirmed the increment of chloride binding with exposure period and IER was the dominant ingredient at this chloride binding. Bound chloride content was increased with increase of IER percentage and 3% ion exchange resin mixed specimens showed highest amount of bound chloride content in all tested specimens, compared with control and other specimen. This phenomenon was observed both in HESPC and PC. Thus, these results proved the significant usage of admixture for increasing chloride binding in concrete. Once chloride ions penetrate into the mortar specimens and contact with the resin, they effectively absorb chloride ions, exchanging hydroxyl ions into the pore solution and fix them into their beads consistently. It results in reducing free chloride ions in the pore solution and hence decreasing the chloride induced deterioration. It also increases the alkalinity of the cement matrix and ultimately reduces the corrosion probability of concrete structures.

3.2 EPMA

Chloride ion absorption and distribution in the cement mortar specimens were also obtained through EPMA technique. The EPMA results of ion distribution after 84 days for PC were shown in Figure 4. The EPMA



Figure 4. Chloride ion distributions after 84 days for PC in (a) & (b)

was done only for the specimens containing 0% and 3% IER which revealed that, due to the containment of IER in the cement mortar, the accumulation of much amount of chloride has been observed in test specimens than control specimens. The images clearly depicted the chloride absorption and binding phenomena due to the existence of resin admixture. As already discussed that IER has a wonderful capacity of absorbing and binding of chloride ions when comes in contact with them. In this case, chloride ions penetrated into mortar specimens by diffusion process and absorbed into the resin beads. In case of control specimen although it did not contain resin admixture also showed a little amount of chloride accumulation and absorption. This accumulation was possible due to the penetration of chloride inside the specimen just for concentration and veloci-

ty gradient. This EPMA showed the phenomena of much amount of chloride accumulation inside the specimen due to the existence of resin into the mortar specimen which was also observed in potentiometric titration analysis. So the EPMA also confirmed and validated the same phenomena of chloride movement and absorption by IER as observed in potentiometric titration analysis.

4 CONCLUSIONS

According to the analysis and results obtained by potentiometric titration method and EPMA, some major conclusions can be derived: Firstly, in case of titration analysis, it was revealed that accumulation and absorption of chloride ions inside the mortar specimen was a direct function of resin (admixture) contents, i.e, much the resin contents, much the chloride absorption and binding both in HESPC and PC. The inconsistency which was observed in the results also might be due to improper curing, moisture condition, w/c ratio, delay of cement hydration and slight variations in exposure conditions. Secondly, the experimental results of the chloride content were validated by EPMA analysis and the same phenomena was observed and confirmed by EPMA. And finally, it can be concluded that, 84 days is not so much time to understand the phenomena at all. So, further investigations with much effective observation and time trend might give a more realistic and rational results. As it was observed that existence of resin in mortar specimen could absorb and bind chloride inside the structures, it could ultimately reduce the chloride concentration at reinforcement area. So this Ion Exchange Resin admixture might be potentially and effectively useful in reducing and restraining chloride induced corrosion in RC structures in coastal areas or in marine environment.

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