

# Renovate RC structures with newly developed mortar, considering chloride binding and inverse diffusion phenomenon

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## Abstract

In Japan, many RC bridges and infrastructure along the coast line have been deteriorated due to ingress of chloride ions. The objective of this study is to develop high durable repair mortar with ion-exchange resin as an admixture to enhance life span by eliminating chloride ion from existing RC structures. And as a part of the objective, this paper discusses the effectiveness of typical commercially available anion exchange resin in preventing chloride induced corrosion within concrete by using its excellent ion-exchange and binding ability, though its real effectiveness with concrete is not still clearly identified. A number of immersion tests were conducted using small mortar specimens mixed with ion-exchange resin and high-early strength Portland and blast furnace slag cements. The volume contents of ion-exchange resin were 1.0, 2.0 and 3.0%. The specimens were immersed into 10% sodium chloride (NaCl) solution for one day and then exposed in drying condition for 6 days. These exposure procedures were repeated for 28, 56 and 84 days. Then total and free chloride contents at various depths in all tested specimens were measured in each time period. The inverse diffusion test was conducted with mortar specimens casted with high-early strength Portland cement maintaining 10% chloride ion only up to 8 cm while top 2 cm casting with 3% ion exchange resin mixed mortar. Total chloride was measured in four consecutive depths after 28 and 140 days. Test results showed the significant enhancement of chloride binding in newly developed mortar with ion-exchange resin compared to normal mortar. The linear relationship between free and bound chloride was also noticed in all specimens, irrespective to the cement types. The absorption of chloride by ion-exchange resin was further increased with increment of chloride concentration in order to achieve its optimum capacity. At last, the effective adsorption of chloride from matured concrete by newly developed repair mortar, using outward movement (inverse diffusion), was clearly observed.

**Keywords:** Reinforcement corrosion, chloride attack, ion-exchange resin, renovate RC structures

# 1. Introduction

Corrosion of reinforced concrete structures is a major problem throughout the world, demanding significant amounts for repair and rehabilitation (Batis et al., 2003). Steel in concrete is normally protected from corrosion by the passive film formed at the steel-concrete interface in an alkaline cementitious matrix. However, depassivation can occur either when the pH of the pore solution drops to low values due to carbonation or when chloride ions (from de-icing salts or from sea water) have penetrated in to the reinforcement in sufficient quantities to destroy the protective oxide layer. Corrosion in the form of rust formation and loss in cross section of the rebar will then start in the presence of oxygen and water (Elsener B., 2002). The repair of damaged RC structures can be made using a new range of ready-mixed mortars (Batis et al., 2003). These materials may consist of polymer-modified mortars or may be prepared using different kinds of additives, such as silica fume or fly ashes. These substances can be added as admixtures to mortar or can be directly applied on concrete surface. Any inhibitor should have good solubility characteristics in concrete to reach the metal corroding surface rapidly. In addition, the physical and durability properties of concrete should not be adversely affected. In the present study, one of typical commercially available anion exchange resin has been examined with different cement types to produce high durable mortar for renovation of RC structures. This ion-exchange resin admixture is prepared as spherical beads of 0.50mm in diameter and used in powder form after regenerating it into the hydroxyl form. It has a cross linked polystyrene structure that is designed to give an optimum balance of capacity and regeneration efficiency. Further it is insoluble substance containing loosely held ions which are able to be exchanged with other ions in solution which come and contact with them. These exchanges take place without any physical alteration to the ion exchange. Thereby the ion exchange resin absorbs and binds chloride ions from the existing concrete and liberates hydroxyl ions into the pore solution. This action results in both reduction of free chloride and enhances the alkalinity of the pore solution by re-passivating the steel reinforcement. This paper presents the efficiency of the repair mortars' barrier effect with its higher chloride binding ability and the outward chloride movement phenomenon from existing concrete, using immersion test and inverse diffusion tests respectively.

## 2. Test Method

### 2.1 Materials and mix proportions

One of the typical commercially available anion exchange resin (AMBERLITETM IRA402 Cl), type 1 strongly basic, clear gel, 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 60% (Cl form) with 660 g/L-R apparent density. The reversible swelling in chloride form to hydroxyl form is nearly 30% and the regenerated resin was used as powder at the experiments. High early-strength Portland cement (HPC) and 40% ground granulated blast furnace slag replaced with ordinary Portland cement (BFS) were also used in this study. Their physical properties and chemical compositions are listed in *Table 1*. The series of test specimens with their materials and mix proportions are also listed in *Table 2*.

Table 1: Physical properties and chemical compositions of materials used in the tests

Materials	Density (g/cm <sup>3</sup> )	Specific Surface area (cm <sup>2</sup> /g)	Chemical composition (% by mass)							
			LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Cl
HPC	3.14	4510	1.06	20.0	5.01	2.79	65.9	0.80	2.94	0.012
BFS	3.04	3920	1.30	25.46	8.67	1.96	54.82	3.53	2.27	0.015

Table 2: Series of test specimens and their mix proportions at immersion test (kg/m<sup>3</sup>)

Specimen Type	Cement	Water	Sand	Admixture
S1:HPC (control specimen) & S5:BFS (control specimen)	586	293	1259	0
S2:HPC mixed 1% admixture & S6:BFS mixed 1% admixture	586	293	1248	11
S3:HPC mixed 2% admixture & S7:BFS mixed 2% admixture	586	293	1238	21
S4:HPC mixed 3% admixture & S8:BFS mixed 3% admixture	586	293	1227	32

## 2.2 preparation of test specimens and curing conditions

The 10cm x 10cm x 10cm cement-mortar specimens with 0.5 water/cement ratio have been tested at immersion test. At the end of casting, all specimens cured by wrapping in wet cloth film to avoid a leaching out of chloride ions from the cement matrix. This curing procedure was applied to the HPC and BFS specimens for 14 days and 28 days respectively until achieving the required compressive strength. Five sides of the specimen were then sealed by epoxy paint so that the chloride penetration can occur only in one-direction. Immediately after sealing, all cubes were exposed to chloride penetration regime, consisting of 1 day of ponding in 10% sodium chloride (NaCl) solution followed by 6 days of drying with constant temperature and humidity of 20 °C and 60% RH respectively. All specimens were exposed to a total of 12 cycles in steps of 28 days, 56 days and 84 days. At the end of exposure regime, specimens sliced into the layers as 0 to 10 mm, 13 to 23 mm, 26 to 36 mm & 39 to 49 mm. After that, each layer was grounded separately to obtain dust samples, which was then sieved into the 150 µm sieve in fineness and the powders thus obtained were used for chloride analyses. The 10g of collected powder was mixed with 100ml, 1mol/l nitric acid and stirred for 10 minutes using magnetic stirrer to extract acid-soluble chlorides which are mostly equivalent to total chlorides. Further, 20g of collected powder was also mixed with 100ml distilled water and stirred for 24h using magnetic stirrer to extract water-soluble chloride which is mostly equivalent to free chloride. Then, both samples were filtered separately through filtering papers and chloride concentration was measured using potentiometric titration against silver nitrate.

The 10cm x 10cm x 10cm HPC mortar specimens with 0.5 water/cement ratios have been examined in Inverse diffusion test. Initially, up to 8cm of the specimens were casted using cement-mortar mixed with 2.5kg/m<sup>3</sup> chloride concentration. After 1 day of casting, the specimens were demolded and cured by wrapping in wet cloth film as in the immersion test. Wetness of the wrapped cloth film was maintained by spraying water for 28 days. After this period, remaining 2cm layer in all specimens were casted with newly developed mortar mixed with 3% ion-exchange resin. For the comparison, few specimens were made with HPC mortar, without mixing admixture. Then specimens were kept in constant temperature and humidity of 20 °C and 60% RH for 28 and 140 days respectively. At the end

of desired periods, the specimens were sliced into the layers and dust samples obtained to measure the total chloride contents in each layer as mentioned in the immersion test.

### 3. Test results and discussion

The change of total chloride content with penetration distance in mortar specimens after 84 days was shown in Figure 1. The remaining depths except surface layer expanded and showed in the same figure to clear analysis. It shows the amount of chloride consistently decreased with increase of distance from top exposed surface of the specimens. However, total chloride at the surface layer (0 to 10 mm) was considerably high compared with other depths. It may be due to either its close proximity to the ponding surface or surface defects such as blow holes, voids and cracks during the drying periods. The results of remaining depths except the surface layer were therefore considered for the analysis. Consistent with the results, total chloride present in all depths increased with increment of admixture percentage in all specimens. For instance, specimens S4 and S8 with 3% admixture showed the largest amount of chloride in all depths. The control specimens (S1 and S5) showed the least amount of chloride at every depth and the remaining specimens, S2 and S3 were in extent between specimens S1 and S4, as we expected. Thus, it clearly represents a relationship between admixture percentage and increment of chloride content in all depths. Slight increment of total chloride in BFS specimens was noticed by compared with HPC specimens.

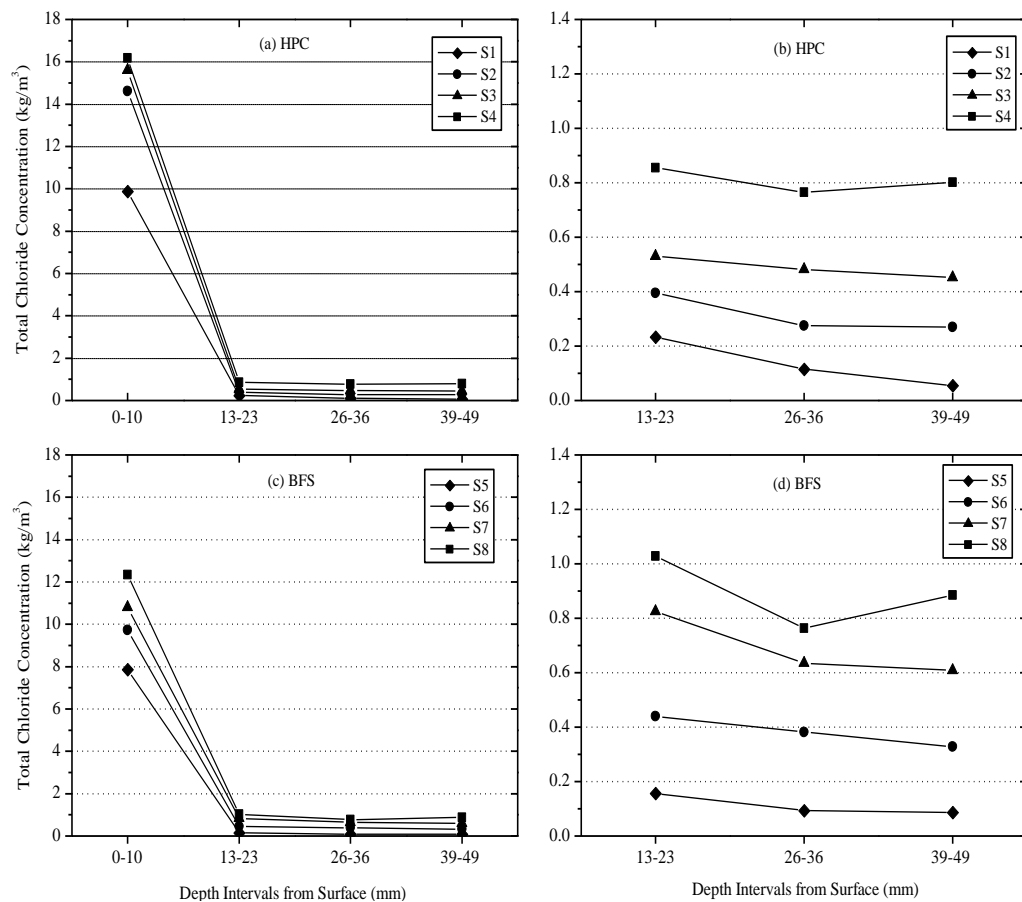
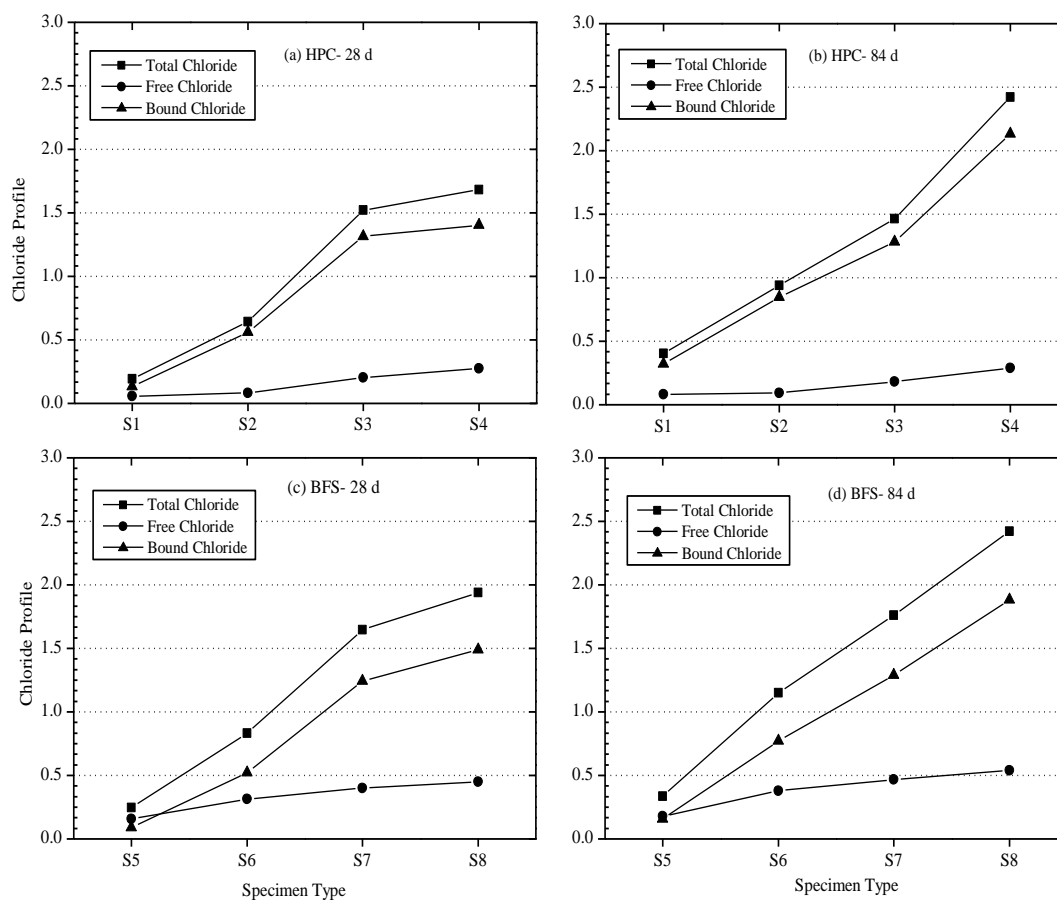


Figure 1- Total chloride content at various depths in (a) HPC and (c) BFS

The change of bound and free chloride profiles compared with total chloride in HPC and BFS specimens at 28 and 84 days were shown in Figure 2. Cumulative total, bound and free chloride in tested specimens were calculated by adding results of investigated depths together, except surface layer. The results clearly confirm that the amount of bound chloride in all specimens was significantly increased with increase of admixture percentage, irrespective to the cement types. Further, chloride binding in all specimens was increased with the time concerned. Considering all HPC specimens, 87% of total penetrated chloride were bound by S4 specimen within 28 days and were raised to 93% within 84 days. At the same time, the free chloride concentration in the pore solution was decreased from 13% to 7%. The BFS specimens initially showed a slight reduction of chloride binding, about 77% of total chloride as bound chloride in S8 specimen. However, it increased with time reaching 87% at the end of 84 days while decreasing free chloride from 23% to 14% with the time. In this chloride binding, newly mixed ion-exchange resin admixture plays a dominant role. The 83% of total bound chlorides were captured by ion exchange resin admixture in S4 specimen and this was raised to 91% in S8 specimen at 84 days. Thus, these results prove the significant usage of admixture for increasing chloride binding. 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 reducing free chloride ions in the pore solution and hence decreasing the chloride induced deterioration. Further, this action causes to enhance alkalinity in pore solution by increasing hydroxyl ions inside the mortar.



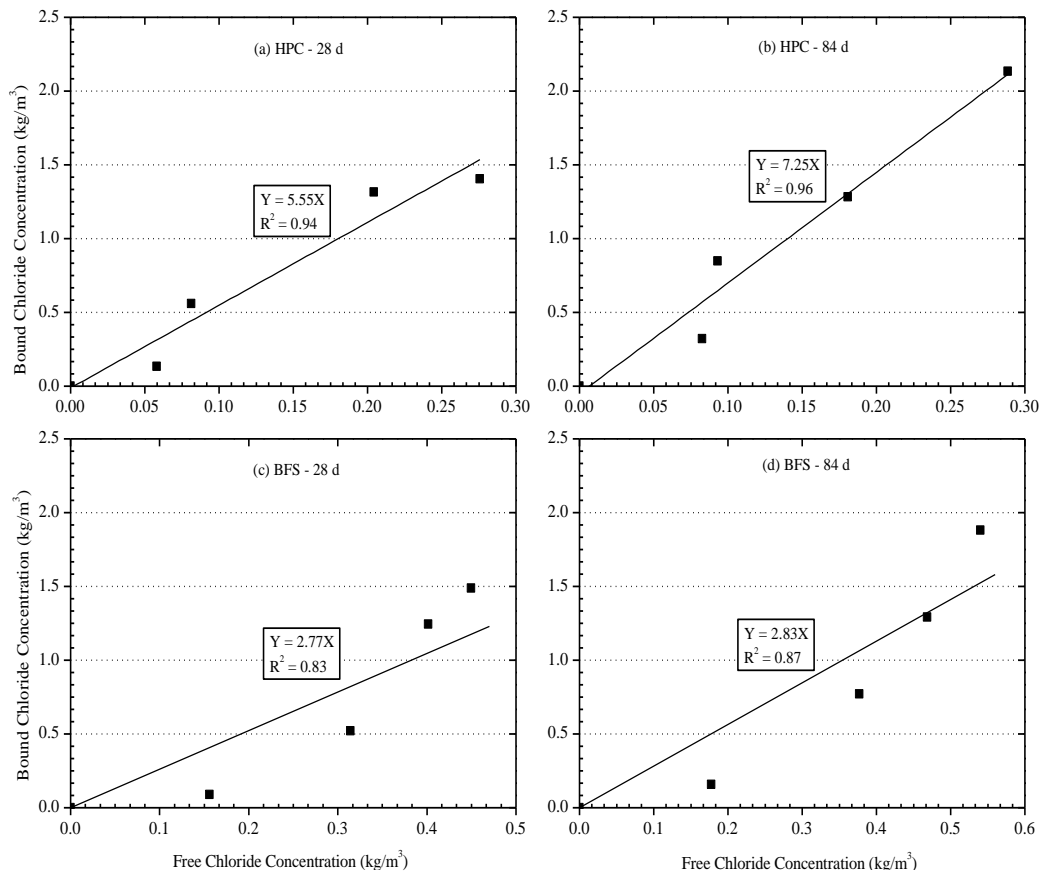
**Figure 2- Chloride profiles in (a) HPC-28days, (b) HPC-84days, (c) BFS-28days & (d) BFS-84 days**

According to the JSCE (2007), threshold chloride ion concentration for corrosion onset is generally taken as  $1.2 \text{ kg/m}^3$ . Considering the results, it shows that the total chloride content within the mortar was exceeded this limit in all circumstances. However, in HPC specimens, over 90% of penetrated chloride were remained as bound chloride and hence the free chloride content which directly participate to the corrosion process, in the mortar were lower than the threshold level. In case of the BFS specimens, approximately 80% of total chloride was remained as bound chloride and it shows a slight reduction than HPC. Considering all cases, a minimal amount of free chlorides in pore solution due to excellent chloride binding, is clearly evident, even though the total chloride ions exceeded the corrosion threshold level.

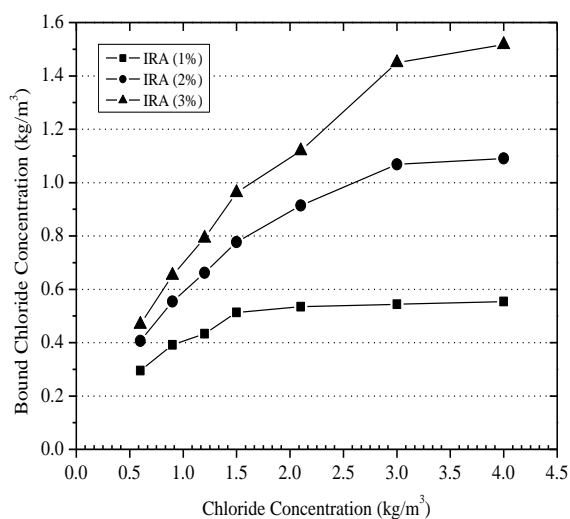
In Portland cement, chloride ions generally combine with the unhydrated aluminates phases and form Friedel's salt (Delagrave et al., 1997). Recent studies have clearly established that chlorides can also be interacted with the calcium silicate hydrates (C-S-H) by chemically and physically (Beaudoin et al., 1990). Blast furnace slag blended cements suffer low early age strength development, which further causes more significant problems such as chloride penetration and potential cracking at an early age. Accordingly, chloride penetration in BFS specimens increased at the early age than HPC specimens. Further, ground granulated blast furnace slag replaced with Portland cement, modifies the microstructure of cementitious paste and generates more capillary pores in concrete, filled with low density C-S-H gel than Portland cement. It further reacts with water in alkali environment and then with calcium hydroxide to form cement hydration product through pozzolanic reaction. It results to form extra C-S-H gel in the paste (Arya et al., 1995). Thus, once chlorides penetrate to the concrete, C-S-H gel effectively adsorbs the free chloride. In contrast, the higher alumina content in the cement-slag phase also reacts with the penetrated chloride and results in formation of more Friedel's salt in the concrete. However, this phenomenon did not occur in the tested BFS specimens. As mentioned earlier, around 9% of chlorides bound by cement hydrates and it was almost double in HPC specimens. The chloride binding is normally increased with curing time. The blast furnace slag cement also takes more time to complete its slow reactions. Thus, the increment of both curing period and testing period may result to increase chloride binding in BFS specimens.

However, 100% of chloride binding did not occur, at all levels of total chloride, meaning that free chloride was produced at any concentration of total chloride. According to the results, it clearly shows that concentration of free chloride was minimal contrasted with penetrated chloride within the mortar specimens. Thus, the higher chloride binding indicates the lower concentration of free chloride in the pore solution, which reduces the risk of steel corrosion in concrete. According to the results, initially free chloride concentration was slightly increased with admixture percentage in all specimens. The admixture absorbs and binds them continuously and therefore, it may reduce with time. The relationship between free and bound chloride ions over a range of chloride concentrations at a given temperature are known as the chloride binding isotherms. The change of bound chloride content with free chloride content in all tested specimens is represented in Figure 3. The results in above graphs show a linear relationship between free and bound chloride for both cement types in all tested periods. Mohamad and Hamada (2003) also found that there was a linear relationship between free chloride and bound chloride in concrete based on several long-term, ranging from 10 to 30 years, by conducting exposure tests under marine environment for high early strength Portland cement and ground granulated blast furnace cement. However the chloride binding by cement compounds was taken into concern and hence any admixture was not used for above mentioned analysis. Thus, once

the ion-exchange resin is mixed into the mortar, the linear binding relationship remains in constant with time by increasing its' binding capacity. According to the Figure 3, the slope of the line represents the binding capacity of newly made mortar with ion exchange resin admixture. The correlation factor of linear behavior in HPC specimens was almost equal to 1, and it was slightly less in BFS specimens. It may due to lack of time for getting precious data to make clear this linear binding behavior.



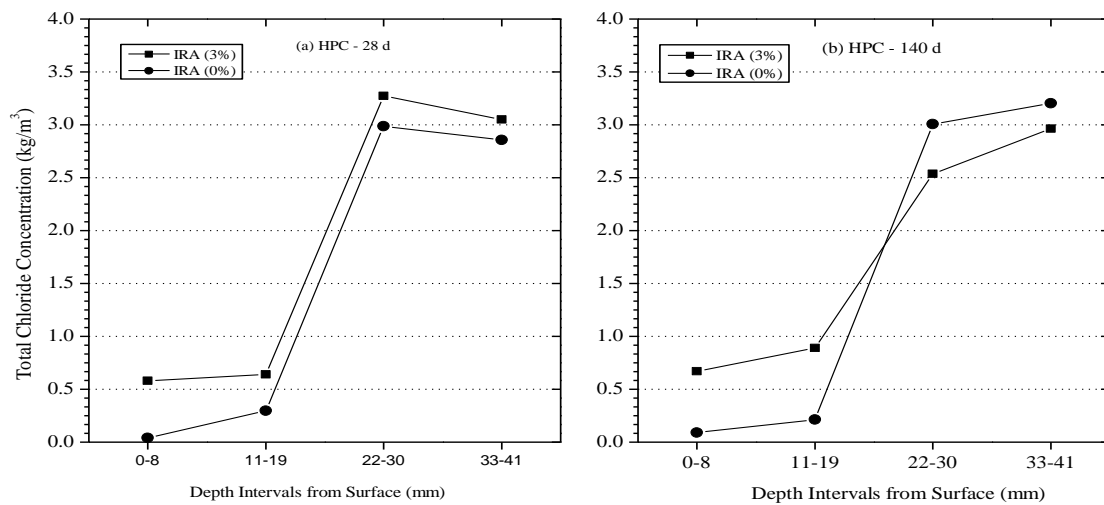
**Figure 3- Chloride binding isotherm in (a) HPC-28 days, (b) HPC-84 days, (c) BFS-28 days and (d) BFS-84 day's specimens.**



**Figure 4- Relationship between bound and total chloride concentration**

The effectiveness of the ion-exchange resin admixture (IRA) was also investigated using different chloride solutions mixed with ion exchange resin in various concentrations (without use of cement types) and the results of the analysis are shown in Figure 4. According to the graph, the bound chloride concentration was gradually increased with increment of chloride concentration in all cases. Once ion-exchange resin reaches to its maximum binding capacity, halts further chloride binding occurrence. Thus, amount of bound chloride doesn't change with chloride concentration after reaching to its optimum capacity. It can be seen in the results of 1% resin mixed mortar

specimen. The results also show a linear relationship between bound chloride and total chloride content in all cases before achieving their maximum binding capacity.



**Figure 5- Inverse diffusion behavior of chloride at (a) HPC-28 days and (b) Hpc-140 day's specimen**

The outward movement of chloride ion from existing matured concrete structures to newly added repair mortar layer through the diffusion process (inverse diffusion) was simulated in the laboratory using small cement-mortar specimens. Initially we focused our attention to high early strength Portland cement and Figure 5 represents the results obtained from the study. The higher concentration gradient between newly casted mortar layer and the remaining part of the specimen allow diffusing chloride ion outward. Thus a slight increment of average velocity and fewer amounts of chloride ion entering the newly developed mortar layer (0-19mm) by diffusion can be observed in specimens even without the admixture. Once admixture is mixed with the newly casted mortar layer (0-19mm), it significantly adsorbs chloride from mature part of the specimen and bind them into the resin beads. This process continuously occurs in all layers and thus the chloride ions in the mortar specimen gradually move into the newly casted mortar layer mixed with admixture. This can be clearly identified by comparing the results of 22-41 mm zone along with time.

After 28 days of casting, test results show the total chloride content within the 33-41 mm layer was slightly reduced in the admixture mixed specimen, compared with other type. However, this was completely changed with time and the chloride content within that layer was dramatically reduced in admixture mixed specimen than normal mortar specimen. It may result due to adsorption and fixing of chloride ions by the ion exchange resin and allow more chloride to move outward the specimen. Considering the results, the chloride content in 0-19mm layer of admixture mixed specimen shows a higher chloride concentration, than the other layer without admixture at 140 days. As a result, the chloride concentration around the reinforcement depth may reduce in the specimen and hence reduce the deterioration speed due to chloride attack.

The order of affinity for anions contain in the cement paste (HPC) has been examined and the results were tabulated in Table 3. Partially regenerated (80% of OH<sup>-</sup> ion with 20% of Cl<sup>-</sup> ion) ion-exchange resin has been used in this analysis, to identify the exchange behavior in different types of ions. The ion-exchange resin admixture has an order of affinity for common anions and the corresponding list for amine based anion exchangers is OH<sup>-</sup><HCO<sub>3</sub><sup>-</sup><Cl<sup>-</sup><Br<sup>-</sup><NO<sub>3</sub><sup>-</sup><HSO<sub>4</sub><sup>-</sup><PO<sub>4</sub><sup>3-</sup><CrO<sub>4</sub><sup>2-</sup><SO<sub>4</sub><sup>2-</sup>.



Table 3: Amount of ion content absorbed by ion-exchange resin in HPC cement paste

Type of Cement	Amount of ion-exchange resin mixed (kg/m <sup>3</sup> )	Amount of ion concentration absorbed by ion-exchange resin (mg/L)		
		Sulphate ion (SO <sub>4</sub> <sup>2-</sup> )	Chloride ion (Cl)	Nitrate ion (NO <sub>3</sub> <sup>-</sup> )
High early strength Portland cement (HPC)	0%	4000	< 250	< 250
	2.5%	3700 (43%)	< 250	< 250
	5.0%	5100 (30%)	420 (2.4%)	< 250
	10.0%	6000 (17%)	550 (3.1%)	< 250

The HPC cement matrix contains a small amount of sulphate ion, either forms of HSO<sub>4</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup>. Thus, once ion-exchange resin is mixed with mortar, the sulphate ion in the cement matrix exchange with hydroxyl ions which contained in the resin. Therefore, the adsorbing sulphate ions into the admixture rather than removing chloride from the pore solution may occur in the concrete. This process may continue until finishing the sulphate ion adsorption in the cement paste and hence the cements with high concentration of sulphate may delay or prevent the removal of chloride from the concrete. Considering the results of Figure 5, there is a possibility that the sulphate ion obstructed the ion-exchange reaction between chloride and the hydroxyl ions. Thus, the sulphate free cements may enhance the reaction of admixture by eliminating this obstruction.

## 4. Conclusions

According to the analysis, the following major conclusions can be derived:

1. The increment of total chloride in all depths is a direct function of the absorption and binding capacity of admixture in all tested specimens. The total chloride content present at any given depths thus increase with increment of admixture percentage in mortar.
2. Newly mixed ion-exchange resin admixture significantly increases the chloride binding ability in mortar instead of other binding agents (unhydrated aluminates phases and C-S-H gel). Test results confirm that more than 80% of bound chloride captured by the ion exchange resin admixture and the remaining were fixed by others.
3. Linear relationship between free chloride and bound chloride was identified in the analysis. Hence the newly developed mortar mixed with ion-exchange resin admixture follows a linear binding isotherm. The increment of bound chloride with chloride concentration also noticed and at last, it was constant once the admixture reached to its optimum binding capacity.
4. Newly made mortar with higher binding capacity and inverse diffusion concept can be used to eliminate free chloride from existing concrete structures. However, the ion-exchange process obstruct by sulphate ions of the cement paste and thus, it slightly delays the chloride removal process.

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