Fundamental study on the state of chloride ion at different depth from the surface of concrete

M. Shinichiro[1] and T. Iyoda[2] and T. Uomoto[3]
[1] *Graduate Student, School of Eng., Shibaura Institute of Technology, Japan*
[2] *Assistant professor, Shibaura Institute of Technology, Japan*
[3] *Professor, Public Works Research Institute, Japan*
E-mail: m509090@sic.shibaura-it.ac.jp

ABSTRACT: Chloride-induced corrosion of steel bar is a big problem for reinforced concrete structures, so it is necessary to understand the chloride ion diffusivity for predicting the durability of structures. There are two types of chloride ions: free and bound ions. The bound chloride ion is furthermore classified into Friedel's salt and adsorbed ions. Generally, it is believed that the free chloride ions influence diffusivity. In this research, Friedel's salt content and generated period were measured with X-ray diffractometry (XRD) and the ratio of Friedel's salt to total chlorides was evaluated. Next a new method was developed for measuring free chloride ions, and it was suggested that free chloride ions and bound chloride ions could be classified by combining XRD and the new method. Future works should aim to estimate the durability of reinforced concrete structures by using this examination's result.

1. INTRODUCTION

Durability of concrete structures is affected by the penetration of chloride ions carried by seawater and sea breeze. Chloride ions contribute to corrosion of steel bar, which is a big problem for reinforced concrete structures. It is necessary to understand the diffusivity of chloride ions in order to predict the structure's durability. As shown conceptually in Figure 1, there are two types of chloride ions: free and bound ions. The bound chloride ion is further classified into Friedel's salt and adsorbed ions. Generally, it is believed that free chloride ions influence the diffusivity and there are suggestions for chloride ion diffusivity tests and chloride ion classification methods; however, those methods cannot consider the relationship between the chloride ion state and depth from concrete surface. The diffusivity at the surface and inside concrete is thought to be different due to the influence of factors such as curing, water-cement ratio, cement type and fineness, therefore it is important to understand the relationship between concrete depth and chloride ion state. This research aims to establish a method for classifying the state of chloride ion and clarify the diffusivity and its influencing factors. From the first test, the relationship between submersion period and ratio of Friedel's salt to total salt was investigated by X-ray diffractometry (XRD). Next, a new method for understanding the relationship between depth from surface concrete and ratio of the free chloride ion to total salt was developed.

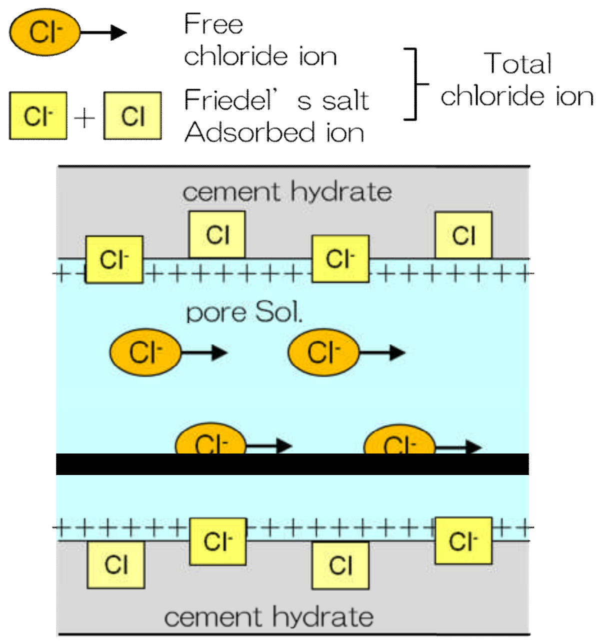

Figure 1 Conception diagram of the chloride ion in concrete

2. X-RAY DIFFRACTOMETRY TEST (XRD)

2.1 Experimental outline

The XRD test was performed to understand the generation limit quantity and generation speed of Friedel' s salt which is influence factor of bound chloride ion. Table 1 shows the cement paste mix proportions for XRD test. Materials for mixing were prepared and stored at 20℃ for 24 hours before casting, and the cylinder specimens (φ100×200mm) were made from cement paste. Table 2 shows the curing method and period, and the specimens were examined after submersion in salt waters with differing salinity. Friedel's salt was measured by XRD-Rietveld method, and the software used for Rietveld analysis was TOPAS (Bruker AXS). The phases that were quantified were Friedel's salt, calcite, gypsum, bassanite, portlandite, etringite (Ett), mono-salfate (Ms), monocarbonate (Mc), hemiccarbonate (Hc), depending on the specimen, as well as basic minerals such as alite (C_3S), belite (C_2S), cubic-C_3A, orthorhombic-C_3A, and C_4AF. The amount of total chloride ions was examined by [Method of test for chloride ion content in hardened concrete (JIS A 1154 : 2003)] of the Japanese Industrial Standards.

Table 1 Mix proportions

	W/C	W	Binder	
			OPC	BFS
	(%)	(g)	(g)	(g)
OPC	50	30	60	
BB			30	30

Table 2 The curing method and submersion period

Kind of cement	Curing (day)	Salinity (%)	The dipping period of the salt water (day)	
OPC and BB	Water curing 7day	0.0	7	28
		1.0		
		3.0		
		5.0		
		10.0		
		15.0		
		20.0		

2.2 Result of XRD test

Figure 2 shows the relationship between Friedel's salt content (%) and the submersion water salinity. In both periods, Friedel's salt was generated more for blast-furnace slag cement than for Portland cement. After 7 days submersion, Friedel's salt tended to increase with increase in salinity. However, at 28 days the Friedel's salt content remained the same even at different salinity levels. Figure 3 shows the relationship between total salt (kg/m^3) and the submersion water salinity. Total salt tended to increase with increase in salinity and submersion period. Therefore, after 28 days submersion it was thought that only free chloride ion content increased because the Friedel's salts content remained constant.

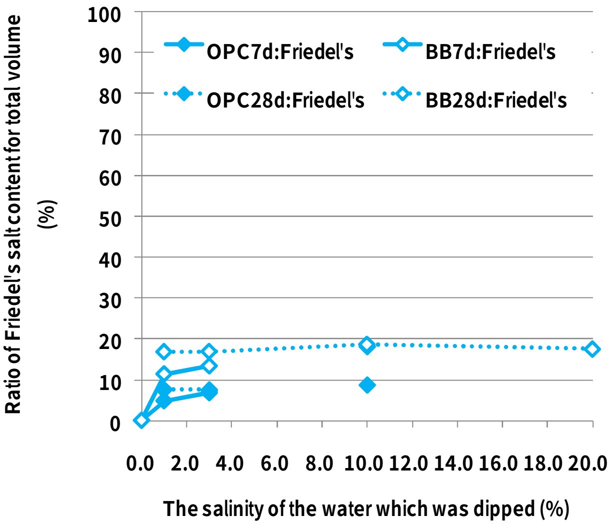

Figure 2 Relationship between Friedel's salt content (%) and the salt's density (%) of the water which was dipped

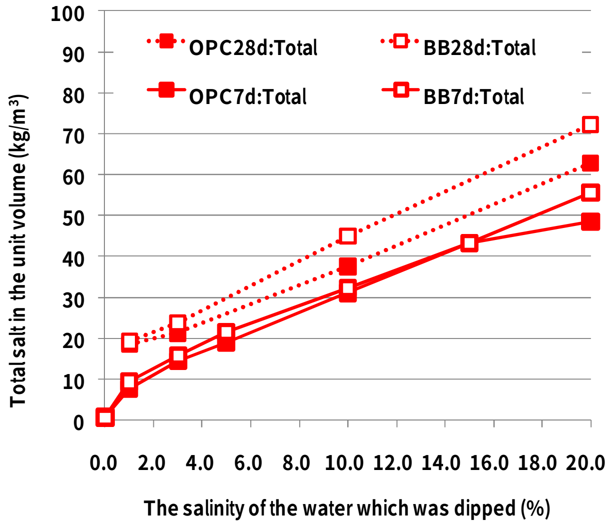

Figure 3 Relationship between total salt (kg/m^3) and the salt's density (%) of the water which was dipped

3. Free chloride ion test

3.1 Method and principle

The process for identifying free chloride ion is as follows.

1. Cylinders specimens (φ100×200mm) were prepared and the top and bottom 10mm were cut off in order to remove the influence of bleeding.
2. The specimen sides were covered with epoxy resin to prevent water penetration, and one open side was submerged dipped in 3% salinity water (similar to seawater salinity).
3. In the experiment period, the specimen is cut every 10mm.
4. Those specimens were placed in a cell following JSCE standard "Test method for effective diffusion coefficient of chloride ion concrete by migration". Figure 4 shows a conceptual diagram of the examination device.
5. Voltage is applied by DC regulated circuit and the salinity of the cell on the positive pole side is measured over a given time period.
6. Once the salinity becomes constant the chloride content of the positive pole side is calculated from the salinity. This chloride content is evaluated as the free chloride ion in the specimen.
7. After this examination, the specimen is crushed and its chloride content is measured by the conventional method in the JIS standard "Method of test for chloride ion content in hardened concrete, JIS A 1154:2003". This content is evaluated as the bound chloride ion in the specimen.
8. The total chloride content is calculated as the sum of the free chloride ions and bound chloride ions.

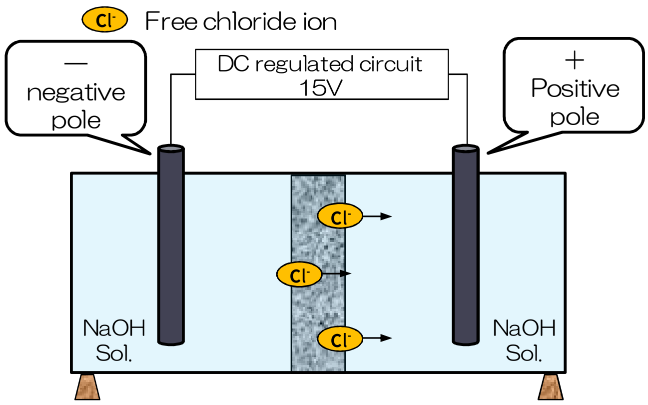

Figure 4 The conception diagram of the examination device

3.2 Examination to identify precision

To confirm the precision of the examination, specimens were prepared under similar conditions. Materials for mixing were prepared and stored at 20℃ for 24 hours before casting. The specimens were mortar cylinders (φ100×200mm), and cured by water curing for 7 days, then submerged for 28 days in salt water with 3.0% salinity. Next, these cylinders were cut every 10mm, and one specimen was examined by conventional method and the other examined according to the process explained in 2.1.1. Figure 5 compares the results of the conventional method and the new method. Total chloride content measured by the conventional method was equal with the sum of free and bound chloride ions and examined by the new method. It was suggested that free chloride ions and bound chloride ions could be classified by this new method.

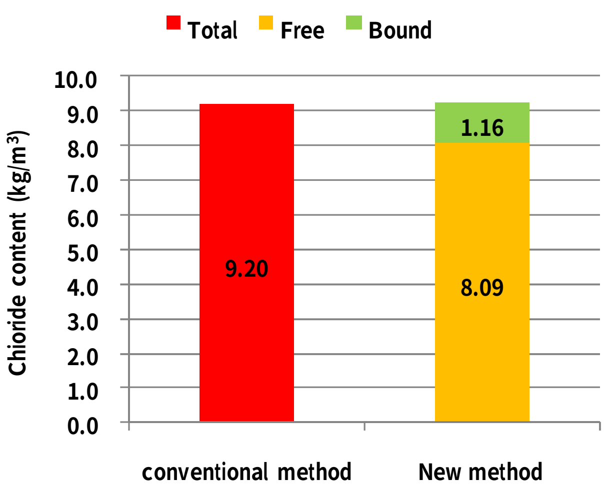

Figure 4 The comparison result of a conventional method and a new method

Using the XRD test result for OPC:28d, bound chloride ions were classified as Friedel's salt and adsorbed chloride ion. Figure 5 shows the results combined the new method with the XRD test data. In Portland cement (OPC), ratio of a free chloride ion for total salt was high. Also the bound chloride ion was occupied in the adsorbed chloride ion. Therefore it is thought that the diffusivity of chloride ion is influenced by the adsorbing factor such as pore structure, pH and surface electric potential.

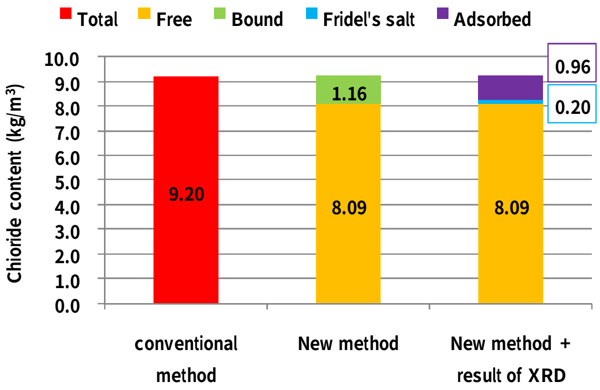

Figure 5 Result of combining the new method with the XRD test data

4. CONCLUSION

This research aimed to establish a method for measuring free chloride ions, and tried to understand the generation of Friedel's salt. The conclusions of this study are as follows.

1. Friedel’s salts generated by both Portland cement and blast-furnace cement after 28 days reached a limit that was not affected by salt density.
2. Results using the new method correlated well with results obtained by the conventional method, and it was suggested that free chloride ions and bound chloride ions could be classified using this new method.

In the future, it is planned to understand the relationship between depth from the concrete surface and state of chloride ion using the new method developed here.

5. REFERENCES

[1] JSCE, 2007. Japan Standard Specifications for Concrete Structures, 119-120.

[2] Tetsuya ISHIDA, Shigeyoshi MIYAHARA and Tsuyoshi MARUYA, "Cl binding capacity of mortars made with various Portland cement and admixtures", Journal of the Japan Society of Civil Engineers E, Vol.63 No.1, 14-26, Japan. (in Japanese)

[3] Tsuyoshi MARUYA, Somnuk TANGTERMSIRIKUL and Yasunori MATSUOKA. "Modeling of choloride ion movement at the surface layer of hardened concrete", Journal of the Japan Society of Civil Engineers No.585/V-38, 79-95, 1998.2, Japan. (in Japanese)

[4] S. Okazaki, T. Yagi, T. Kishi and T. Yajima, 2006, Difference of sensitivity due to curing condition on strength and permeability, Cement Science and Concrete Technology, NO.60, 227-234, Japan Cement Association. (In Japanese)