# Study of immobilization mechanism of chloride ion with different concentration of chloride ion using cement with powder admixtures

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# ABSTRACT

Generally, verification of chloride ion penetration in concrete is carried out using a salt immersion test with varying chloride ion concentrations. However, the chloride ion penetration mechanism is still unclear, particularly considering that the chloride ion concentration is different for cements with different powder admixtures, such as blast furnace slag, fly ash, and silica fume. In this research, the immobilization mechanism of the chloride ion on the concrete surface was investigated using XRD measurement of the surface area and of milled total samples. Furthermore, the immobilization mechanism at various depths of 0.5 mm increments was also examined using XRD analysis. As a result, it was found that the immobilization mechanism is different for each type of admixture, and that, for the cements using with fly ash and blast furnace slag, the accelerated test can represent the actual conditions even with different chloride ion concentrations.

# 1. Introduction

Salt damage is one of the serious causes of deterioration in reinforced concrete. This phenomenon is triggered when the chloride ion content at the reinforcement position in the concrete exceeds the amount of the corrosion limit. Chloride ion content in concrete is classified into two types. One is the integrated chloride ion originally contained in the concrete material, and the other is the chloride ion supplied from the external environment, such as seawater and de-icing salt. The amount of integrated chloride ions can be adjusted by controlling the used materials. However, the penetration of external chloride ions is largely dependent on the supply from the saline environment, but it has also been known to be highly dependent on the void structure and the chloride ion adsorption and immobilization characteristics of the concrete.

The salt immobilization capacity is known to vary greatly depending on the type of admixtures used, such as ground granulated blast furnace slag (BFS), fly ash (FA), silica fume (SF), and lime stone powder (LSP). This study will attempt to clarify the effect of admixture through several approaches. First, cementitious materials using various

admixtures will be subjected to the salt immersion test, and the immobilization performance of each material and its immobilization mechanism will be examined. The salinity immobilization capacity at various depths will also be measured, which will make it possible to classify the salt penetration mechanism for each admixture. Next, the immobilization capacity under immersion in different salt concentrations using ordinary Portland cement (OPC) and BFS cement will be compared. This makes it possible to quantitatively measure the salt immobilization capacity at different salt concentrations. Finally, the applicability of the accelerated test will be studied using the immersion test method with higher chloride ion concentrations and various admixtures. The results should provide comprehensive information for proper material selection considering the salt damage mechanism.

## 2. EXPERIMENTAL OUTLINE

## **2.1 Experimental samples**

The experimental program was conducted in two stages. In the first stage, the immobilization capacity and the mechanism of chloride ion immobilization for various admixtures was examined. In the second stage, the examined mechanism were confirmed by carrying out immersion tests for OPC and BFS cement with different chloride ion concentrations, as well as measuring the immobilization capacity of chloride ion at various depths. In both stages, the cement used was OPC, with the composition as shown in Table 1. In Stage 1, cementitious materials using BFS, FA, and LSP admixtures (compositions are given in Table 1) were prepared with an OPC replacement ratio of 20%, as shown in Table 2. In Stage 2, OPC and BFS cement were used (the replacement ratio of BFS was 50%), which reflects the general purpose cements used in Japan. In both stages, the prepared cement pastes had a water-to-binder ratio of 0.50. The cement paste was molded into a plastic petri dish of the size  $\phi 52 \times 8.6$  mm. They were then kept in a sealed state using polyethylene film. After curing to an age of 28 days, the polyethylene film of the top surface was removed, but the plastic petri dish was not removed for use in the immersion test. In Stage 1, they were immersed in a solution of 5% chloride ion concentration, while in Stage 2 they were immersed in various solutions of 0.5%, 3% and 10% concentrations.

	Chemical component(%)								Density	Fineness						
	ig.loss	insol.	$SiO_2$	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	$SO_3$	Na <sub>2</sub> O	$K_2O$	$TiO_2$	$P_2O_5$	MnO	Cl	$(g/cm^3)$	(cm <sup>2</sup> /g)
OPC	0.61	0.07	20.94	5.45	2.83	64.96	1.54	2.05	0.32	0.48	0.27	0.31	0.08	0.03	3.16	3490
BFS	0.17	-	34.05	14.65	0.32	43.15	5.94	-	0.26	0.28	0.57	0.01	0.33	-	2.91	4280
FlyAsh	1.67	-	55.25	30.23	4.53	2.32	0.93	0.38	0.89	0.45	1.87	0.14	0.03	-	2.25	3900
LSP	44.06	-	0.09	0.05	0.03	55.71	0.30	-	0.00	0.00	0.02	0.02	0.01	0.00	2.77	6100

 Table1 Chemical component of the tested materials

Table 2 Miz	x proportions	in	test stage 1
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	Binder content (weight %)					
	OPC	BFS	FlyAsh	LSP		
OPC	100	-	-	-		
OPC-BFS		20	-	-		
OPC-FA	80	-	20	-		
OPC-LSP		-	-	20		

#### 2.2 Analysis of immobilized chloride ion

In Stage 1, measurement of the samples in the chloride ion solution was conducted after 1, 7, and 28 days of immersion. Measurements were conducted on the surface layer and on samples from the milled test specimens. Stage 2 focused on the degree of penetration from the surface for the various concentrations. The immersion period for each concentration is shown in Figure 1, and the method for grinding the 0.5 mm incremental depths from the surface is shown in Figure 2. In both stages, the samples were analysed by X-ray diffraction. The target of the measurement was to analyse the hydration products (mainly ettringite, monosulfate and carbonate-based hydrate) and the immobilized chloride ions (Kuzel's salt and Friedel's salt). The internal standard method was used for quantification.





Figure 1 Measurement method and measurement age in stage 2

**Figure 2 Testing procedure** 

# 3. EXPERIMENTAL RESULTS

## 3.1 Comparison of the immobilization ability of various admixtures (Stage 1)

Figure 3 shows the XRD analysis results before and after 1, 7, and 28 days immersion in chloride ion solutions for the cement pastes using various admixtures such as BFS, FA and LSP. In OPC, the generation of monosulfate and ettringite can be confirmed before immersion in the chloride ion solution, and the generation of Kuzel's salt immediately after

immersion (1 day) can be confirmed. Furthermore, over the immersion period, it is recognized that Kuzel's salt is converted to Friedel's salt. In the long term (28 days), there are only ettringite and Friedel's salt. For the cement-based materials including BFS and FA, the amounts and production rates of Kuzel's salt and Friedel's salt are different, but the generation process (mechanism) was confirm to be the same as that of the OPC only.

On the other hand, for the cement-based material with LSP, the formation of ettringite and mono-carbonate before immersion was confirmed, but monosulfate could not be seen before immersion. In addition, the generation of Friedel's salt could be seen immediately after immersion, but generation of Kuzel's salt was not observed. Therefore, it was concluded that the generation process is different for cementitious materials containing LSP. Consequently, based on these results, the product flows for salt immobilization for each admixture are shown in Figure 4. It is proposed that the mechanism of salt immobilization may be different depending on the formation of mono-carbonate.



Figure 3 XRD analysis results before and after chloride ion solution immersion for different admixtures



# Figure 4 Image of material flow for immersion in chloride ion solution

# **3.2** Comparison of immobilization ability at various depths from the surface (Stage 2)

In order to further understand the salt immobilization mechanism under different salt immersion concentrations, tests were performed to investigate the product at selected immersion ages and at various depths using OPC and BFS cement.

## (1) Immobilization mechanism at various depths

Figures 5 and 6 show the measurement results for Kuzel's salts and Friedel's salt at various depths for the samples immersed in the 3% concentration solution. First, focusing on the Kuzel's salt, for both the OPC and BFS cement, it can be seen that the amount of Kuzel's salt in the surface layer is greater after 2 days of immersion compared to 1 day. In addition, it can be seen that the peak of the Kuzel's salt production moved to deeper position as the immersion period grew longer. Furthermore, the deepest position at which Kuzel's salt is detected in OPC is deeper than that for the BFS cement. Consequently, it is understood that the salt penetration is prevented at the surface layer of the BFS cement, as the amount of Kuzel's salt production is greater in OPC.

Next, the results of the Friedel's salt are examined. In both the OPC and BFS cement, it can be confirmed that the amount of Friedel's salt increased with immersion age, similar to the Kuzel's salt. In addition, generation of Friedel's salt at deeper points for longer immersion times can be confirmed. The greatest depth at which the generation of Friedel's salt was found for BFS cement was 2mm, but for OPC it was detected at 3.5 mm. It can be seen that BFS cement can contribute to greater resistance against salt penetration and immobilization.



Figure 5 Results for Kuzel's salt progress (left: OPC, right: slag cement)



Figure 6 Results for Friedel's salt progress (left: OPC, right: slag cement)

Therefore, at a given depth, when chloride ions are penetrating into concrete, first Kuzel's salt is produced, followed by chloride ion immobilization, which changes Kuzel's salt into Friedel's salt. To understand why BFS cement reduces the salt penetration depth compared to OPC, the following two points are considered. First, the dense pore structure suppresses the penetration of chloride ions. Second, as immobilized salts such as Kuzel's salt or/and Friedel's salt are generated at or near the surface, the salt does not penetrate further into the concrete. To further investigate these points, it is necessary to also measure the pore structure of hardened cement pastes in addition to the immobilization behavior.

## (2) Effect of chloride ion concentration on the immobilization mechanism

Next, the generation mechanism and generation depth of Kuzel's salt and Friedel's salt for OPC and BFS cement immersed in different chloride ion concentrations were compared. Figure 7 shows the depth of production of Friedel's salt (integrated intensity of the XRD) for different chloride ion concentrations after three days of immersion. When the concentration is higher, generation of Friedel's salt at a deeper position was found for both cements. In addition, the amount of Friedel's salt is higher for higher concentration. However, the depth of penetration was suppressed in the BFS cement, as compared to the OPC.

Furthermore, most of the chloride ion immobilization occurs close to the surface layer, as was discussed previously in section 3.2(1). BFS cement was shown to strongly prevent the chloride ion penetration, so the total amount of Friedel's salt and the deepest position of Friedel's salt (Friedel's salt formation depth) were examined more closely. The amount of Friedel's salt increases at higher concentrations, and the greater the amount of salt supplied, the larger the generation amount becomes. It is also noted that Friedel's salt is supplied at greater depths for OPC compared to BFS cement (Figure 7). When comparing the chloride



# Figure 7 Results for Friedel's salt progress for different chloride concentrations

ion penetration depth in OPC and BB, it can be seen that there is greater penetration from the surface in the OPC specimen, and the trend becomes more notable as the chloride ion concentration increases. Thus, when compared to BFS cement, for OPC the salt gradually penetrates deeper from the surface layer and increases the amount of Friedel's salt at greater depths, so it can be concluded that the performance of OPC for preventing chloride ion penetration is not as high as BFS cement.

In order to examine the relationship between the chloride ion concentration and the generation of Kuzel's salt and Friedel's salt, the generation speed was calculated for each of the test cases. The method for calculating the generation speed is as follows. For Kuzel's salt, it is difficult to calculate the generation speed from the amount of Kuzel's salt because Kuzel's salt changes to Friedel's salt, so the generation speed was calculated from the relationship between the immersion time and the deepest position where Kuzel's salt was observed. On the other hand, for Friedel's salt, the generation speed was calculated from the amount of Friedel's salt and the immersion period. The calculation results are shown in Figure 8. The generation speeds linearly increased with the chloride ion concentration. It is confirmed that BFS cement has a slower generation speed compared to OPC, and, consequently, it has a slow permeation rate. It is thus believed that the results at high concentrations reproduce the results at low concentrations.

The ratio of the calculated coefficients are shown in Table 3. The value at a chloride ion concentration of 0.5% was about 0.43 times the 3% concentration, and the value for the case of 10% chloride ion concentration was between 3.5 and 4.0 times, and this result was not influenced by the type of cement. In other words, when using either OPC or BFS, magnification effect in the accelerated environment is relatively the same, and reflective of the normal environment. Therefore, in both cements, it is considered that the same phenomenon of salt penetration is proceeding, but it will be necessary to examine other admixtures such as LSP and SF.



Table 3 Calcurated accelarated ratio						
	concentration of CI					
	0.50%	10%				
OPC_Kuzel	0.44	3.45				
OPC-BFS_Kuzel	0.43	3.71				
OPC_Friedel	0.22	4.07				
OPC-BFS_Friedel	0.43	4.07				

\* generation speed ratio of these phase by 3% chloride ion concentration

Figure 8 Calculated generation speed

## 4. SUMMARY

The results obtained in this research are summarized as follows.

- (1) When examining the chloride ion immobilization mechanism with various admixtures, the mechanism for the LSP mixture was different from that of the mixtures using the OPC, BFS and FA.
- (2) When examining the immobilization mechanism at different depths using OPC and slag cement, more products of immobilized chloride ion were found at the surface layer of the slag cement samples.
- (3) Finally, when examining the immobilization mechanisms with varying chloride concentrations, the immobilization mechanism was confirmed to be unchanged regardless of chloride ion concentration.

In the future, it is also necessary to consider the use of silica fume and to evaluate the pore structure as related to chloride penetration.

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## REFERENCES

- Tetsuya I., Shigeyoshi M., and Tuyoshi M. (2007). "CL BINDING CAPACITY OF MORTARS MADE WITH VARIOUS PORTLAND CEMENT AND ADMIXTURES", Journal of JSCE E, Vol.63, No.1, pp.14-26
- Shigeyoshi M., and Tuyoshi M., Tetsuya I. (2006) "STUDY FOR METHOD OF QUANTITIVE ANALYSIS OF BINDING CHLORIDE ION IN MORTARS", *Proceedings of the Japan Concrete Institute, Vol.28, No.1, pp.893-898.*