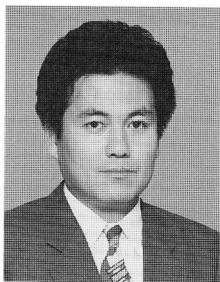


## DURABILITY ASSESSMENT OF BINDERS BY ANALYZING LIQUID AND SOLID PHASE

(Reprinted from Transaction of JSCE, No.478, V-21, 1993)



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### SYNOPSIS

In order to assess durability of binders, authors have analyzed liquid and solid phase of mortar specimens made from ordinary Portland cement, fly ash, blast furnace slag and silica fume which have been mixed. Liquid phase was analyzed by the method of measuring ion concentrations in pore solution. Solid phase was analyzed by powder X-ray diffraction and differential thermal analysis. Specimens were sealed cured and submerged in saturated NaCl solution. The results were obtained as follows. The trinary mixture of cement, flyash and slag is most durable to alkali-aggregate reaction because alkali ion concentration of pore solution is the lowest. The trinary mixture is most durable to salt contamination because chloride ion concentration from environment is lowest. Friedel's salt was synthesized and observed by an electron microscope.

**Keywords:** pore solution, alkali ion, chloride ion, binary mixture, trinary mixture

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1. INTRODUCTION

Concrete comprises air, solid, and liquid phases. In these phases, the liquid phase is a field where several chemical reactions take place, and is a channel where chloride ions move from the surface to the bottom. Therefore the chemical study of concrete is effected by the method of expressing pore solution and measuring several ion concentrations. The method of expressing pore solution was devised by Longuet et al. [1] and was improved by Barneyback et al. [2]. Using this method, the pore solution can be expressed by putting a mortar or paste specimen into a special device and subjecting it to high pressure. The theme of the study with this method is mainly durability of cement concrete, such as the elucidation of the mechanism of alkali aggregate reaction [3, 4] and the influence of binders on fixing chloride [5, 6].

The objective of this study is to assess the durability of binders against alkali aggregate reaction and chloride contamination. Alkali aggregate reaction is the reaction between alkali ions dissolving to liquid phase from binders and aggregate, an expansive gel adsorbing water being produced [7]. So it is important to clarify the change of alkali content and alkali ion concentration. The resistance to alkali aggregate reaction was estimated by the new index showing the influence of the type of binder on the decrease of alkali ion concentration in pore solution. The resistance to salt contamination was estimated by investigating the influence of the type of binder and of the curing duration on chloride penetration using mortar specimens. The durability of binders was assessed by powder X-ray diffraction method, thermal analysis and ignition loss measurement in addition to the analysis of the liquid phase.

The types of binder assessed in this study were ordinary Portland cement, a binary mixture of ordinary Portland cement and fly ash, a binary mixture of ordinary Portland cement and blast furnace slag, a binary mixture of ordinary Portland cement and silica fume, and a trinary mixture of ordinary Portland cement, fly ash, and blast furnace slag.

2. EXPERIMENTS

2.1 Materials and Mixture proportions

The binders used for mortar specimens were ordinary Portland cement (OP), fly ash (F1,F2), blast furnace slag (B1,B2) and silica fume (SF). Toyoura silicious sand (standard sand in Japan) was used as the fine aggregate. Deionized water was used as the mixing water. Table1 shows the chemical analysis of binders based on Japanese Industrial Standard JIS R 5202 and the available alkali content of fly ash was measured by the ASTM C 311 method.

Table 1 Chemical Analysis of Binders

Chemical analysis (weight%)	Ordinary Portland Cement	Flyash		Blast Furnace Slag		Silica fume
	O P	F 1	F 2	B 1	B 2	S F
Ig. loss	0.8	1.27	4.61	2.00	1.36	1.5
Insol.	0.2	76.41	86.31	0.23	1.13	—
SiO <sub>2</sub>	21.6	51.41	59.10	31.02	32.05	94.0
Al <sub>2</sub> O <sub>3</sub>	5.4	24.70	22.56	13.62	12.44	0.3
Fe <sub>2</sub> O <sub>3</sub>	2.6	5.69	4.12	0.36	0.46	0.3
CaO	64.0	8.69	3.99	42.88	43.23	0.2
MgO	1.8	2.00	1.07	6.01	6.39	0.5
SO <sub>3</sub>	2.0	0.49	0.57	0.11	1.56	—
Na <sub>2</sub> O	0.38	1.61	0.93	0.18	0.23	0.4
K <sub>2</sub> O	0.55	1.22	1.16	0.38	0.34	0.8
TiO <sub>2</sub>	0.48	1.28	0.99	0.95	1.67	—
P <sub>2</sub> O <sub>5</sub>	0.13	0.57	0.26	0.02	0.02	—
MnO	0.17	0.07	0.05	0.46	0.32	—
Cl	0.01	<0.01	0.01	<0.01	0.01	—
*Na <sub>2</sub> O	—	0.54	0.36	—	—	—
*K <sub>2</sub> O	—	0.40	0.46	—	—	—

\* available alkalis

Table 2 Mixture Proportions of Mortars

Mix	OP	F1	F2	B1	B2	SF	WA	SA
M0	1	—	—	—	—	—	0.5	2
M1	0.8	0.2	—	—	—	—	0.5	2
M2	0.8	—	0.2	—	—	—	0.5	2
M3	0.5	—	—	0.5	—	—	0.5	2
M4	0.5	—	—	—	0.5	—	0.5	2
M5	0.3	0.2	—	0.5	—	—	0.5	2
M6	0.3	0.2	—	—	0.5	—	0.5	2
M7	0.3	—	0.2	0.5	—	—	0.5	2
M8	0.3	—	0.2	—	0.5	—	0.5	2
M9	0.9	—	—	—	—	0.1	0.5	2
M10	0.8	—	—	—	—	0.2	0.5	2

Table 2 shows the eleven kinds of mixture proportions estimated in this study. The basic mixture proportion is that binder : sand : water is equal to 1 : 2 : 0.5 by weight. In table 2, M0 is ordinary Portland cement only, M1 and M2 are the binary mixture of ordinary Portland cement and fly ash, M3 and M4 are the binary mixture of ordinary Portland cement and blast furnace slag, M5, M6, M7, and M8 are the trinary mixture of ordinary Portland cement, fly ash and blast furnace slag. M9 and M10 are binary mixture of ordinary Portland cement and silica fume, which have different contents of silica fume.

## 2.2 Specimens Preparation, Curing condition and Test period

A 3-liter mortar mixer was used for preparing mortars and the process of mixing mortar was based on Japanese Industrial Standard JIS R 5201. As soon as mortar was mixed, cases made of polypropylene were filled with mortar. The crevice between a cap and a receptacle was sealed by paraffin, named a sealed receptacle.

Two methods of curing were used: the sealed curing (C1) and saturated chloride solution curing (C2). The condition for sealed curing (C1) is a temperature of 20°C in sealed receptacles until testing period. The duration of wet curing for saturated chloride solution curing (C2) was 1, 3, 7, 21 days (C2-1, C2-3, C2-7, C2-21). In wet curing, the cap is opened at one age, the top surface of mortar is filled with deionized water, the receptacle is shut again, and is reserved at a temperature of 20°C. In saturated chloride solution curing, was that mortar specimens were taken out of receptacles and were dipped in saturated chloride solution at a temperature of 20°C.

The testing period in the case of sealed curing is 1, 7, 28, 91, 182, 365, or 1217 days; and in the case of saturated chloride solution curing, 1, 7, 28, 91, 182, or 365 days.

## 2.3 Analysis of liquid phase

### 2.3.1 Expression of pore solution

Three specimens were inserted into the cylinder of the pore solution expression device shown in photograph 1. Pore solution was squeezed out of mortar specimens by imposing a load of about 500 MPa repeatedly. The minimum number for imposing a load was four regardless of the testing age. When about 3 ml pore solution was not obtainable, the number for imposing a load was changed suitably. As soon as squeezing of pore solution came to an end, the syringe filled with pore solution was sealed up to exclude air. Before inserting mortar specimens into pore solution expression device, chloride adhering to the surfaces of the specimens was removed by cleaning with ethanol.

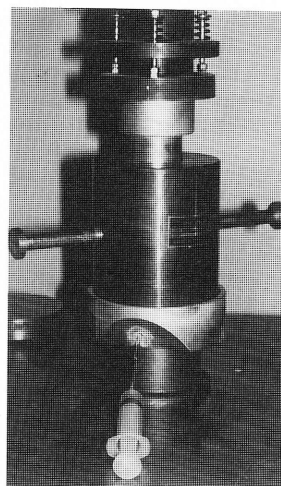


Photo.1 Pore Solution Expression Device

### 2.3.2 Chemical analysis of pore solution

The measurement items of the pore solution are the pH value, and the  $\text{OH}^-$ ,  $\text{Na}^+$ , and  $\text{K}^+$  ion concentrations. The pore solution was percolated using a  $0.2\ \mu\text{m}$  dispofilter and the pH value and  $\text{OH}^-$  ion concentration were measured during the day of squeezing the pore solution. The pH value was measured with a pH-meter, and the  $\text{OH}^-$  ion concentration was calculated as  $P - (M - P)$  [8], where P is the P alkali level (pH = 8.3) and M is the M alkali level (pH = 4.8). Until  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations were measured by atomic absorption electrospectroscopy, 6N-HCl was added to the pore solution to maintain acidity.

## 2.4 Analysis of solid phase

### 2.4.1 Powder X-ray diffraction method and differential thermal analysis

After squeezing the pore solution, specimens were crushed and dehydrated by washing in acetone. Before carrying out powder X-ray diffraction and differential thermal analysis, the powder from the specimens was sifted with a 0.074 mm sieve.

### 2.4.2 Ignition loss

The weight of the specimens (Wod) was measured after removing water by drying at a temperature of  $105 \pm 5^\circ\text{C}$  for one day. The weight of the specimens (Wig) was measured after drying the specimens at a temperature of  $1050 \pm 50^\circ\text{C}$  for two hours. The ignition loss was calculated as  $(\text{Wod} - \text{Wig})/\text{Wod} \times 100(\%)$ .

## 2.5 Synthesis of Friedel's salt

Friedel's salt was synthesized in order to clarify the character of Friedel's salt which fixed free chloride in cement concrete. The procedure of synthesizing Friedel's salt is adding NaCl solution to ettringite, maintaining the value of pH 13 with NaOH and boiling up for one hour. The method of synthesizing ettringite is mixing CaO and  $\text{Al}_2(\text{SO}_4)_3$  ( $\text{CaO} : \text{Al}_2(\text{SO}_4)_3 = 6:1$ , by mol ratio) with adequate water [9]. The ettringite was confirmed by powder X-ray diffraction method. The reason why Friedel's salt was synthesized from ettringite with chloride penetrating into concrete was thought to be that Friedel's salt was came not only from C3A but also from ettringite.

## 3. TEST RESULTS

### 3.1 Results of analyzing liquid phase

The change of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$  ion concentration were shown in figures 1 to 11. In figure 1, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$  increase till 28 days and keep constant value after 28 days in the case of ordinary Portland cement only.

In figures 2 and 3, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$  ion increase till 28 days, decrease after 28 days, and keep constant value at the age of 182 days in the case of binary mixture of ordinary Portland cement and fly ash.  $\text{Na}^+$  ion concentrations decrease little in F1 fly ash, but both  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations decrease in F2 fly ash.

In figures 4 and 5, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$  ion increase till 7 days and  $\text{OH}^-$  ion concentrations keep constant value after 7 days in the case of binary mixture of ordinary Portland cement and blast furnace slag. But the change of  $\text{Na}^+$  and  $\text{K}^+$  ion concentration is different from the kind of blast furnace slag.

In figures 6 to 9, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$  ion in the case of trinary mixture are lower than that in the case of binary mixture, and the change of several ion concentrations is different from the combination of fly ash and blast furnace slag.

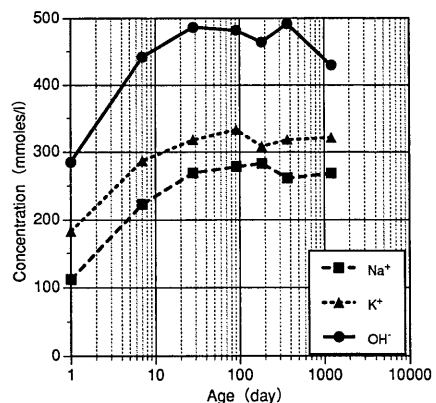


Fig.1 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M0C1

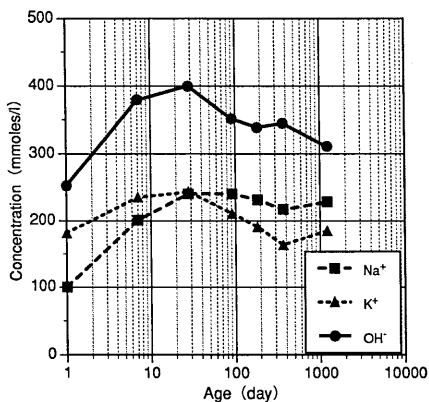


Fig. 2 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M1C1

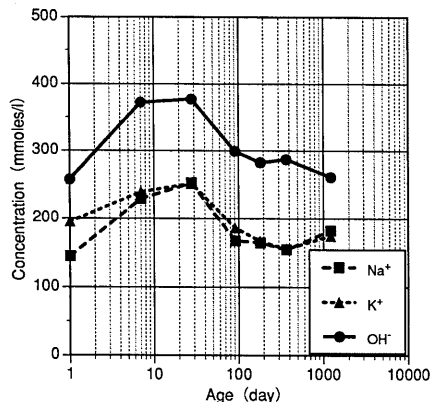


Fig. 3 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M2C1

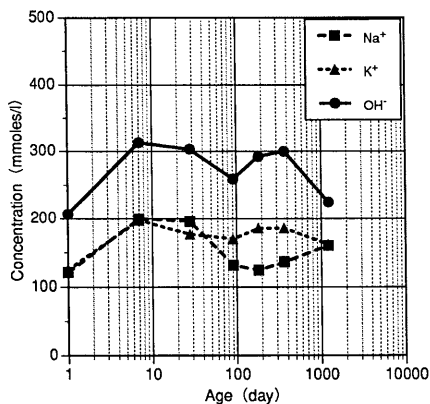


Fig. 4 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M3C1

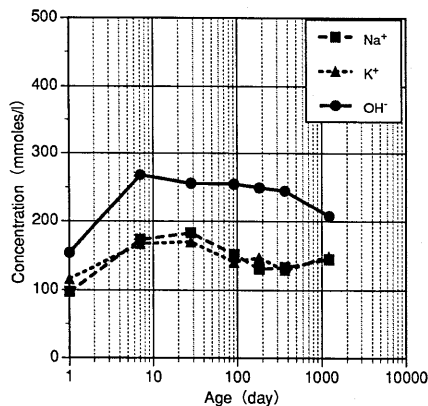


Fig. 5 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M4C1

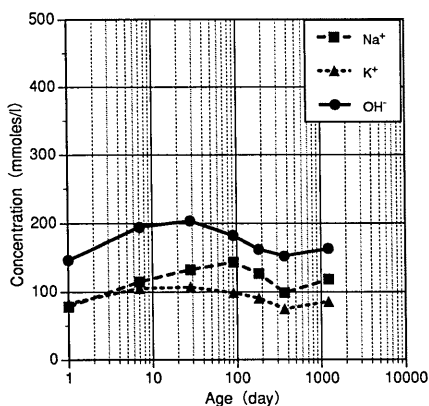


Fig. 6 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M5C1

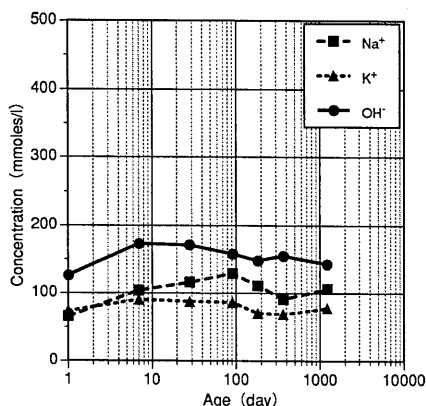


Fig. 7 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M6C1

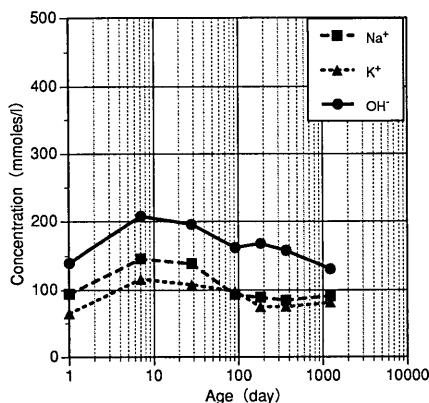


Fig. 8 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M7C1

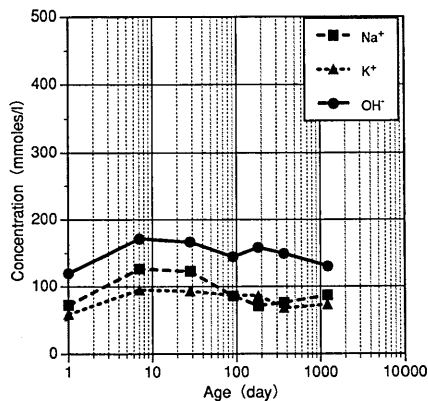


Fig. 9 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M8C1

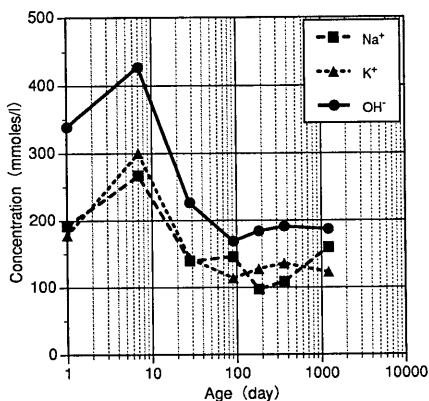


Fig. 10 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M9C1

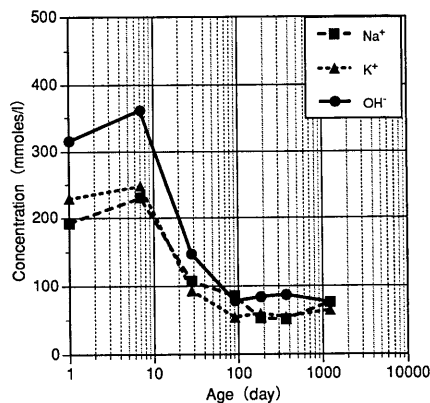


Fig. 11 Measured Concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  ions of M10C1

In the case of the binary mixture of ordinary Portland cement and silica fume shown in figures 10 and 11, the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{OH}^-$  ion are lower in the case of adding larger content of silica fume than that in the case of small content of silica fume. In spite of the content of silica fume, the three ion concentrations increase till 7 days and decrease after 7 days.

The change of chloride ion concentration in the case of saturated chloride solution curing (curing period is 1, 3, 7, 21 days) is shown in figure 12. The change of chloride ion concentrations are shown each period of wet curing in figures 13 to 17.

### 3.2 Results of analyzing solid phase

Figure 18 shows powder X-ray diffraction patterns of ordinary Portland cement only (M0); a binary mixture of ordinary Portland cement and F1 fly ash (M1); a binary mixture of ordinary Portland cement and B1 blast furnace slag (M3); a ternary mixture of ordinary Portland cement, F1 fly ash and B1 blast furnace slag (M5); and a binary mixture of ordinary Portland cement and silica fume (M10) at the age of 365 days in saturated chloride solution curing (in the case of 7 days wet curing) and in sealed curing. Figure 19 shows differential thermal analysis curves in the same case.

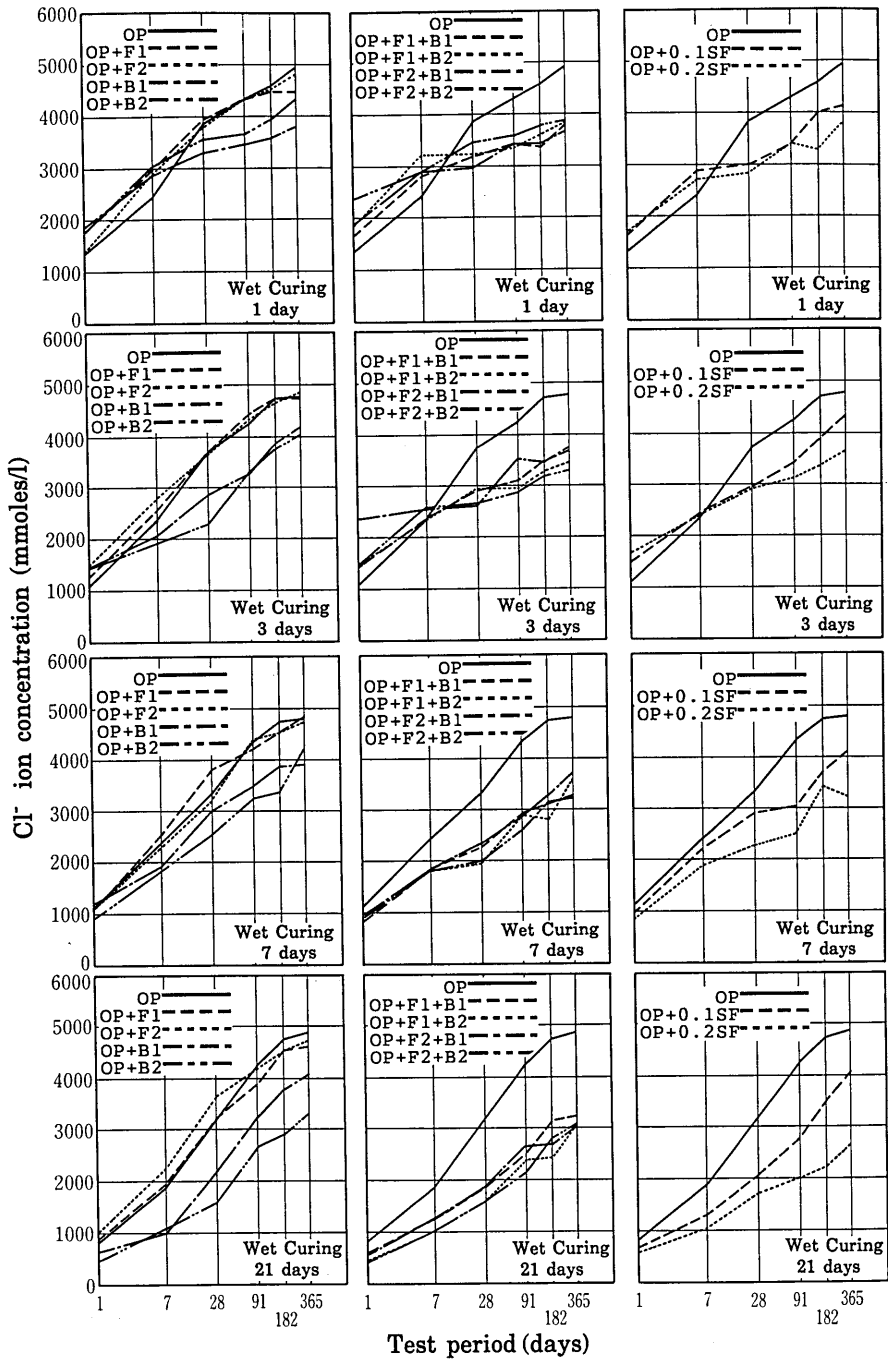


Fig. 12  $\text{Cl}^-$  Ion Concentration of Specimens in Saturated NaCl Solution

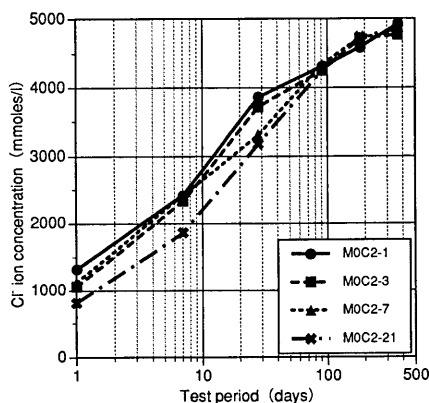


Fig. 13 Cl<sup>-</sup> Ion Concentration of Specimens of M0C2

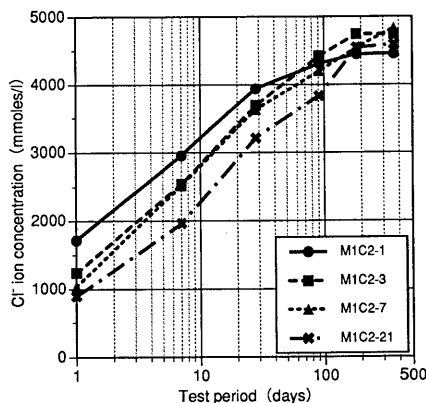


Fig. 14 Cl<sup>-</sup> Ion Concentration of Specimens of M1C2

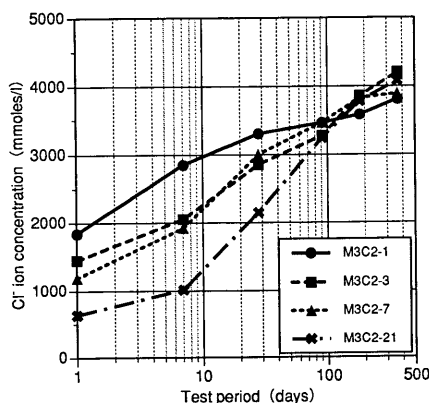


Fig. 15 Cl<sup>-</sup> Ion Concentration of Specimens of M3C2

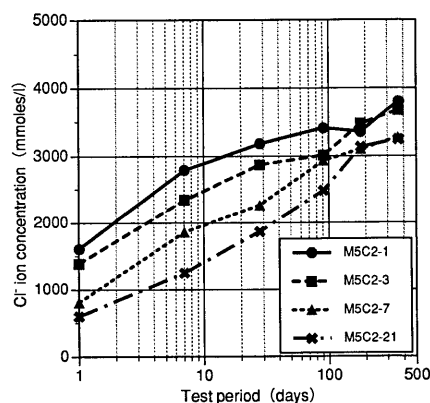


Fig. 16 Cl<sup>-</sup> Ion Concentration of Specimens of M5C2

### 3.3 Results of the synthesis of Friedel's salt

The powder X-ray diffraction patterns and differential thermal analysis curves of Friedel's salt are shown in figure 20. The SEM photograph of Friedel's salt is shown in photograph 2.

## 4. DISCUSSION

### 4.1 The change of alkali ion concentration

It is clear in figures 2 and 3 that OH<sup>-</sup> ion concentration decreases after 28 days in the case of binary mixture using fly ash. This shows that a vigorous pozzolanic reaction takes place after the age of 28 days [3]. Pozzolanic reaction takes place

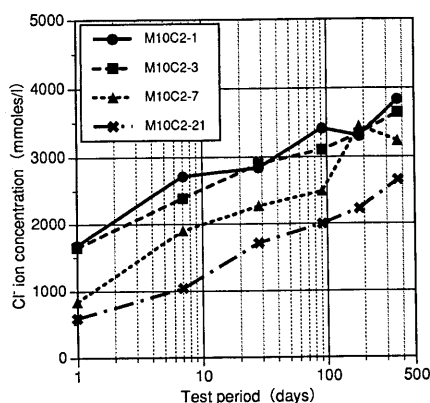


Fig. 17 Cl<sup>-</sup> Ion Concentration of Specimens of M10



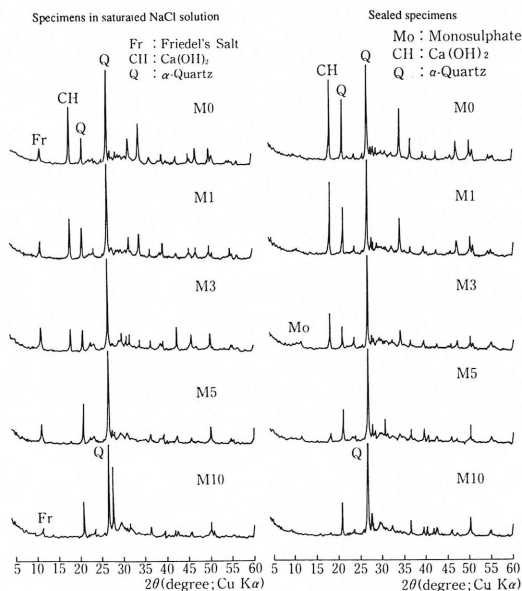


Fig. 18 Powder X-ray Diffraction Patterns

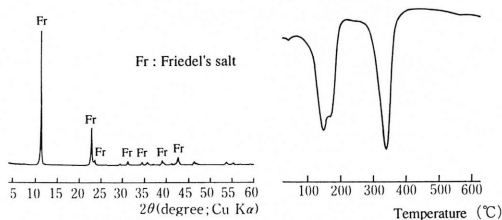


Fig. 20 Powder X-ray Diffraction Patterns and Differential Thermal Analysis of Friedel's salt

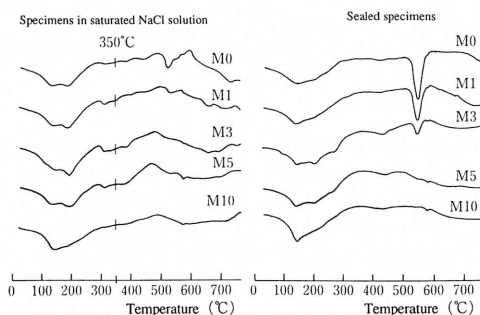


Fig. 19 Differential Thermal Analysis Curves



Photo.2 The SEM Photography of Friedel's salt

Table 3 Decreasing Ion Concentrations of Alkali  
(t = 365 days)

Mix	lg. loss (%)	Wn/C (%)	(mmoles/l)						
			Modified Ion M (X)		Diluted Ion D (X)		Decreasing Ion G (X)		
			Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup> + K <sup>+</sup>
M0	7.8	24.2	135	164	—	—	—	—	—
M1	6.2	18.4	137	103	108	131	29	-28	1
M2	6.0	17.0	102	102	108	131	-6	-29	-35
M3	6.0	17.3	88.9	122	67.5	82.0	21.4	40	61
M4	6.1	17.8	85.7	83.1	67.5	82.0	18.2	1.1	19.3
M9	5.8	17.1	71.7	89.5	122	148	-50	-59	-109
M10	4.9	13.9	36.7	39.4	108	131	-71	-92	-163

Table 4 Decreasing Ion Concentrations of Alkali  
(t = 1217 days)

Mix	lg. loss (%)	Wn/C (%)	(mmoles/l)						
			Modified Ion M (X)		Diluted Ion D (X)		Decreasing Ion G (X)		
			Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup> + K <sup>+</sup>
M0	6.9	20.9	156	187	—	—	—	—	—
M1	5.9	17.4	149	121	125	150	24	-29	-5
M2	6.2	17.8	117	112	125	150	-8	-38	-46
M3	6.8	19.8	96.6	97.8	78.0	93.5	18.6	4.3	22.9
M4	6.6	19.5	88.5	90.9	78.0	93.5	10.5	-2.6	7.9
M9	5.9	17.5	104	80.0	140	168	-36	-88	-124
M10	4.9	13.9	54.9	46.6	125	150	-70.1	-103.4	-174

vigorously after 7 days in the binary mixture of silica fume which is pozzolanic material in figures 10 and 11. It is possible to predict the starting period of pozzolanic reaction from the period of decreasing of alkali ion concentration. The change of OH<sup>-</sup> ion concentration and the kind of alkali ion are different each kind of fly ash and each content of silica fume. It is thought, therefore, that the composition of pozzolanic reactor influences this phenomenon.

OH<sup>-</sup> ion concentrations remain unchanged from the age of 7 days to 365 days in the case of binary mixture of blast furnace slag in figures 4 and 5. So the change of OH<sup>-</sup> ion concentrations in the binary mixture of blast furnace slag is different from that in the case of mixture including fly ash as pozzolanic material. The change of Na<sup>+</sup> and K<sup>+</sup> ion concentrations are different for each kind of blast furnace slag.

Several new assessment index are calculated from Na<sup>+</sup> and K<sup>+</sup> ion concentrations in pore solution and ignition loss, and the influence of binders on the change of alkali ion concentration are assessed. Modified ion concentration (M(X), where X is the type of binder), that is converted from measured ion concentration and hydration rate (Wn/C) calculated is converted from ignition loss as to revise apparental increase of ion concentration by progressing hydration [10]. Modified ion concentration is a conceptional concentration and calculated using equation as follows;

$$M(X) = \{(We/B) / (W/B)\} \times S(X), \quad (1)$$

where We is the evaporable water content in a specimen, B is the unit weight of a binder, W is the unit weight of water and S(X) is measured ion concentration.

In the case of binary mixture, diluted ion concentration (D(X), where X is the type of binder) is calculated, that is the concentration considered dilution of alkali ions from fly ash and blast furnace slag. The method of calculating diluted ion concentration is that the weight ratio of ordinary Portland cement in each binder (D: dilution coefficient) is multiplies by modified ion concentration in the case of ordinary Portland cement only (M(OP)). Decreasing ion concentration, that is a disparity between modified ion concentration and diluted ion concentration, is calculated using equation.

$$G(X) = M(X) - D(X) \quad (2)$$

Decreasing ion concentration is the concentration where alkali ions decrease above the effect of dilution out of pore solution. The model of calculating decreasing ion concentration is shown in figure 21. The result of calculating decreasing ion concentration is shown in table 3 of the mixture case of M1 to M4, M9 and M10 at 365 days and is shown in table 4 at 1217 days. If the sign of decreasing ion concentration is plus, it is indicated that it is no effect of binders on decreasing alkali ion. If the sign is minus, binders have effect on decreasing alkali ion.

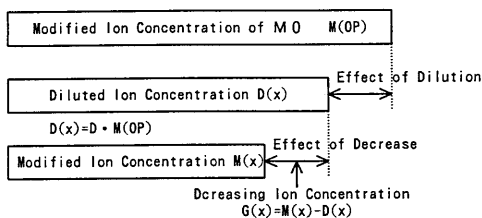


Fig. 21 Model of Calculating Decreasing Ion Concentration

It is shown in tables 3 and 4 that the content of decrease of alkali ion in the case of binary mixture including fly ash is higher than that in the case of binary mixture including blast furnace slag. In the binary mixture with fly ash, the decreasing ion concentration of K<sup>+</sup> ion is the same value in spite of the kind of fly ash.

But the sign of the decreasing ion concentration of Na<sup>+</sup> ions using F1 fly ash is plus and the decreasing ion concentration of Na<sup>+</sup> ions using F2 fly ash is lower than the concentration of K<sup>+</sup> ions. The reason why the decreasing ion concentration of Na<sup>+</sup> ions is different each kinds of fly ash is that the content of K<sub>2</sub>O is the same value despite of the kind of fly ash but the content of Na<sub>2</sub>O of F1 fly ash is higher than that of F2 in table 1. It is thought that the tendency of binding Na<sup>+</sup> ion into pozzolanic materials is more obvious than that of K<sup>+</sup> ion. The decreasing ion concentration of K<sup>+</sup> ion in the binary mixture with blast furnace slag is lower than that in the mixture with fly ash. The tendency of decreasing alkali ion concentration with silica fume is more marked than that with fly ash

or blast furnace and more obvious with more content of silica fume. The modified ion concentration of 20% silica fume is much low.

In the case of a ternary mixture, the decreasing ion concentration is calculated by the same procedure of ternary mixture. In order to clarify the influence of the combination of fly ash and blast furnace slag on decreasing alkali ion concentration, the accumulated ion concentration is used as an assessing index. The procedure of calculating the index is shown in equation.

$$S(FA + BS) = G(FA + BS) - \{G(FA)+G(BS)\} \tag{3}$$

The decreasing and accumulated ion concentrations of M5 to M8 at 365 days are shown in table 5, and that at 1217 days are shown in table 6. It is a distinctive future that the decreasing ion concentration of K<sup>+</sup> ions is lower than that of Na<sup>+</sup> ions. Concerning accumulated ions, the value of M5 mixture proportion including F1 and B1 is lowest and the value of M8 mixture proportion including F2 and B2 is highest. This is because the accumulated effect of fly ash and blast furnace slag on decreasing alkali ion concentration is more obvious than that of the mixture proportions including each fly ash and blast furnace slag. So the mixture of M8 has no accumulated effect.

Modified ion concentrations of alkali ion in pore solution decrease when fly ash, blast furnace slag and silica fume are mixed with ordinary Portland cement. But the tendency of diluting alkali ion of the binary mixture with blast furnace slag is different from that of the binary mixture with fly ash or silica fume. So it is thought that pozzolanic materials bind the alkali ions. The modified ion concentration is considerably low in the ternary mixture, so it is assumed that the ternary mixture can control the alkali aggregate reaction by considering the movement of alkali ion concentrations in the pore solution.

Table 5 Accumulated Ion Concentration of Alkali ( t = 365 days )

(mmoles/l)													
Mix	lg. loss (%)	Wn/C (%)	Modified Ion M(FA+BS)		Diluted Ion D(FA+BS)		Decreasing Ion G(FA+BS)		Σ Decreasing Ion G(FA)+G(BS)		Accumulated Ion S(FA+BS)		
			Na +	K +	Na +	K +	Na +	K +	Na +	K +	Na +	K +	Na + + K +
M5	5.4	15.0	69.1	52.4	40.5	49.2	28.6	3.2	50.4	12.0	-21.8	-8.8	-30.6
M6	4.8	13.2	67.2	51.2	40.5	49.2	26.7	2.0	47.2	-26.9	-20.5	28.9	8.4
M7	5.0	13.0	62.8	55.6	40.5	49.2	22.3	6.4	15.4	11.0	6.9	-4.6	2.3
M8	4.6	11.9	58.3	52.2	40.5	49.2	17.8	3.0	12.2	-27.9	5.6	30.9	36.5

Table 6 Accumulated Ion Concentration of Alkali ( t = 1217 days )

(mmoles/l)													
M i x	lg. loss (%)	Wn/C (%)	Modified Ion M(FA+BS)		Diluted Ion D(FA+BS)		Decreasing Ion G(FA+BS)		Σ Decreasing Ion G(FA)+G(BS)		Accumulated Ion S(FA+BS)		
			Na +	K +	Na +	K +	Na +	K +	Na +	K +	Na +	K +	Na + + K +
M 5	5.6	15.7	80.9	58.6	46.8	56.1	34.1	2.5	42.6	-24.7	- 8.5	27.2	18.7
M 6	5.2	14.5	75.3	55.6	46.8	56.1	28.5	- 0.5	34.5	-31.6	- 6.0	31.1	25.1
M 7	5.7	15.3	63.1	56.6	46.8	56.1	16.3	0.5	10.6	-33.7	5.7	34.2	39.9
M 8	5.3	14.2	62.3	52.8	46.8	56.1	15.5	- 3.3	2.5	-40.6	13.0	37.3	50.3

## 4.2 Binding capacity of chloride

Friedel's salt is well known as a material for binding chloride. In this study, Friedel's salt was synthesized from ettringite, and investigated using powder X-ray diffraction and differential thermal analysis. The absorption peak at 150°C by the method of differential thermal analysis was observed in figure 20. It is said that the peak is at 350°C.

The analysis results for saturated chloride solution curing with 7 days wet curing is now discussed based on the data of synthesized Friedel's salt. The first peak of Friedel's salt by the method of powder diffraction method is observed at 11.2 degree as  $2\theta$  in all cases of mixture proportions in figure 18. But the height of the peak in the mixture with blast furnace slag is higher than the mixture with 20% silica fume. The absorption peak at 350°C of Friedel's salt by the method of differential thermal analysis is observed except for binary mixture of silica fume in figure 19. The reason Friedel's salt is synthesized more with blast furnace slag is connected to the content of alminate phase. The reason little Friedel's salt is synthesized with 20% silica fume is thought to be that the OH<sup>-</sup> ion concentration is low and Friedel's salt tends to decompose [5]. In figure 18 of powder X-ray diffraction method with 20% silica fume, there is no peak indicating Ca(OH)<sub>2</sub>, so Ca(OH)<sub>2</sub> is consumed.

It was clarified that the formation of Friedel's salt was hexagonal and thin plate by the method of SEM [9]. It is thought to be that Friedel's salt has no expansive action if it is hexagonal and thin plate in actual structures.

## 4.3 Resitivity against chloride penetration

The change in Cl<sup>-</sup> ion concentration in the case of ordinary Portland cement only has the same tendency as in that of binary mixture with fly ash. This is believed to be because specimens were not cured until over 28 days, by which time pozzolanic reaction was active. However, resitivity against chloride penetration of fly ash is no more than that of blast furnace slag or silica fume, as the change of chloride ion was same in spite of long duration of dipping. Chloride ion concentrations in the case of a binary mixture with blast furnace slag or silica fume and a trinary mixture are higher than that with ordinary Portland cement only at early age with one or three days wet curing. However, the concentration is lower with over 7 days wet curing. This tendency is distinguished in the case of a trinary mixture and binary mixture with silica fume, and the more silica fume. The reason is thought to be that the structure of mortar matrix becomes minute through pozzolanic reaction.

The reason why the resitivity of chloride penetration in the binary mixture with fly ash is not improved and that in the trinary mixture, including fly ash, is more improved than the binary mixture with blast furnace slag is thought to be that the structure comes to minute by the mutual reaction of fly ash and blast furnace slag and the ratio of fly ash or blast furnace slag to ordinary Portland cement is different from that of binary mixture.

In the case of ordinary portland cement only shown in figure 13, the duration of wet curing gives influence on chloride penetration at an early dipping age and the concentration of chloride ions has no change at a dipping age of 365 days, despite the duration of wet curing. In the case of the binary mixture with fly ash in figure 14, the change of the tendency of chloride ions is the same that of ordinary Portland cement only, the duration of wet curing influences chloride ion concentration at an early dipping age a little and chloride ion concentration at a dipping age of 365 days is low. In the case of the binary mixture with blast furnace slag in figure 15, the longer the duration of wet curing, the lower the chloride ion concentration in the pore solution at early age. But the concentration has no change at a dipping age of 365 days regardless of the duration of wet curing. This concentration is lower than that of the binary mixture with fly ash. In the case of the trinary mixture in figure 16, the duration of wet curing has a larger influence on chloride ion concentration and there is a difference of that in specimens at a dipping age of 365 days. This concentration is lower than that of the binary mixture with blast furnace slag. There is the same tendency in the case of a trinary mixture and binary mixture with 20% silica fume.

The results of this chapter are as follows. In order to give binders adequate resistivity against chloride penetration, wet curing period for more than 7 days is necessary. The resistivity of chloride penetration increases in the following order : ordinary Portland cement only; binary mixture with fly ash; binary mixture with blast furnace slag; binary mixture with 10% silica fume; trinary mixture and binary mixture with 20% silica fume.

## **5. CONCLUSIONS**

In this study, the influence of binders on decreasing alkali ion concentrations in pore solution was assessed by analyzing the liquid phase. The influence of binders and the duration of wet curing on the resistivity against chloride penetration was assessed by the method of analyzing liquid and solid phase, too. In order to assess the influence of binary binders on decreasing alkali ion concentration, modified ion concentration, diluted ion concentration and decreasing ion concentration were used. Modified ion concentration is defined as modifying the measured alkali ion concentration by hydration rate, diluted ion concentration is defined as modifying ion concentration of ordinary Portland cement by weight ratio of several binders to ordinary Portland cement, and decreasing ion concentration is defined as the difference between modified ion concentration and diluted ion concentration. In order to assess the influence of trinary binders, accumulated ion concentration, which shows the mutual effect of fly ash and blast furnace slag, was used as well. The conclusions of this study are as follows:

(1) A binary mixture with fly ash and silica fume influences the decrease in alkali ion concentrations. The reason is thought to be pozzolanic reaction. The alkali ion concentration does not decrease in the case of binders with blast furnace slag. The reason is dissolving of alkali ion from blast furnace slag or promotion of dissolving of alkali ion from ordinary Portland cement. The ion concentration is lower than that of ordinary Portland cement.

(2) Alkali ion concentrations decrease as a result of the mutual effect of fly ash and blast furnace slag in trinary mixture, where alkali ion concentrations do not decrease as much in the case of binders in binary mixture. Modified ion concentrations are low.

(3) Friedel's salt, which binds chloride, was observed in specimens with the condition of salt saturated solution. The content of Friedel's salt is much in the mixture with blast furnace slag and is not so much in the mixture with silica fume, so alminate phase and  $\text{OH}^-$  ion concentration in pore solution are thought to be connected to binding chloride. The formation of synthesized Friedel's salt was a hexagonal and thin crystal by the method of SEM.

(4) In order to give binders adequate resistivity against chloride penetration, the duration of wet curing must be over 7 days. The resistivity of chloride penetration is larger in the following order : ordinary Portland cement, binary mixture with fly ash, binary mixture with blast furnace slag, binary mixture with 10% silica fume, trinary mixture, and binary mixture with 20% silica fume. The effect of the improvement of resistivity of chloride penetration in the case of ordinary Portland cement only and binary mixture with fly ash is less than that with blast furnace slag and silica fume.

(5) The resistivity of fly ash to chloride penetration is improved more by mixing blast furnace slag with it than a long curing of pozzolan reaction.

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