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A Study on New Type Cement for High Durability and Environmental Impact Reduction on Effective Use of Blast Furnace Slag

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ABSTRACT:
In order to reduce the amount of CO_2 gas in cement industry, the use of blended cement is valid. Share of blended cement in Japan, has not changed over last 10 years. One of the reasons is that most of blended cement is blast furnace slag cement type B. Blast furnace slag cement type B is available in a variety of situations, however it have not been able to use effectively characteristics of ground granulated blast furnace slag. In this research, it will be intended to improve the performance of cement was mixed blast furnace slag with fly ash and limestone powder. And various durability tests and hydration analysis were conducted. As a result, in carbonation, the amount of additional is dominant. On the other hand, in alkali-silica reaction, a small amount of fly ash was affected. However, limestone powder has not affected. Moreover, in penetrating chloride ion, resistance was higher in amount of blast furnace slag. However, increasing the amount of limestone powder mixture has been confirmed to obtain a higher resistance to penetrate chloride ion. As a reason, it is cleared that the amounts of mono carbonate hydrate and monosulfate hydrate can significantly affect.
Keywords: Blast furnace slag, CO_2 emission, durability, fly ash, lime stone powder

1. INTRODUCTION

It is necessary to control the amount of discharge of carbon dioxide as a battle against global warming. In the cement industry, it becomes important to control the carbon-dioxide emissions at the time of the clinker manufacture. Therefore, it is necessary to expand the use of mixed cement in the future. In Japan, it is that the most frequently used species of mixed cement is blast furnace slag cement type B. This cement is replaced by the 45% of ground granulated blast furnace slag on normal cement, and it is highly effective in reducing the amount of carbon dioxide emissions. However it has been pointed out that the problem on construction site and the cracking of thermal attack. Therefore, the last 10 years, the share of this cement has remained at about 25% less than the total amount of cement. On the other hand, blast furnace slag cement type C is also commercially available, such as cement powder mixed with at least 60% blast furnace slag. However, it can be said that the problem of poor curing and carbonation has been pointed out. Therefore the current situation is difficult to be widely practical. On the other hand, blast furnace cement type A which is the small amount of blast furnace slag on cement, can be treated in the same manner as ordinary Portland cement and blast furnace slag cement type B. However, it cannot be expected to reduce the amount of carbon dioxide emissions is the only blast furnace cement type A use. In addition, the blast furnace slag powder has characterized by the ASR-resistant and salt resistant, blast furnace cement type A which blast furnace slag mixing a small amount on cement, is possible that this feature cannot be achieved. Therefore, in this study, it tried to improve durability by improving blast furnace cement type A. If the above can be realized, then I t can be used blast furnace cement type A is used to structures normally used by ordinary Portland cement. Reducing the amount of carbon dioxide emissions than the current situation on this thing is possible.

In this study, it was compared the durability of some improvement cements on blast furnace slag type A, we examined the practical improved product. Therefore, it has to prepare a cement powder mixed with a small amount of limestone powder and fly ash to cement mixed with 30% ground granulated blast furnace slag. It was intended to create a mortar using these kinds of cement to understand the compressive strength and some durability. And also it was understand to mechanism for durability, to measure some chemical approach.

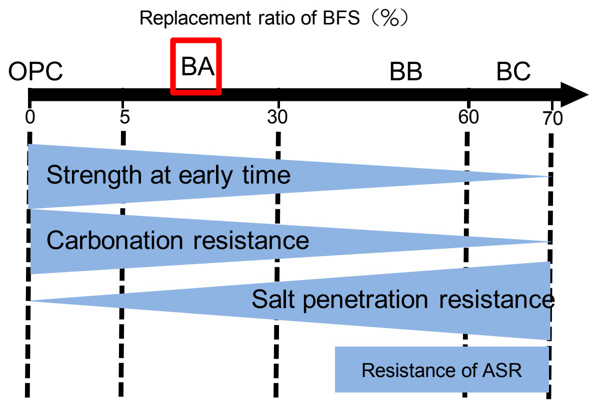

Figure-1 Kind of blast furnace slag cement

Table-1 Cement binder ratio

		Name	Binder ratio (weight %)			
			OPC	BFS	FA	LSP
OPC 100%		OPC	100	-	-	-
BFS 30% replacement		BA	70	30	-	-
BFS 45% replacement		BB	55	45	-	-
FA replace	BFS constant	B30-F3.5	66.5	30	3.5	-
		B30-F7	63	30	7	-
		B30-F14	56	30	14	-
	OPC constant	B25-F5	70	25	5	-
		B20-F10	70	20	10	-
		B10-F20	70	10	20	-
LSP replace	BFS constant	B30-L3.5	66.5	30	-	3.5
		B30-L7	6.3	30	-	7
		B30-L14	56	30	-	14
	OPC constant	B25-L5	70	25	-	5
		B20-L10	70	20	-	10
		B10-L20	70	10	-	20

2. EXPERIMENTAL OUTLINE

It has to prepare a cement powder mixed with a small amount of limestone powder and fly ash to cement mixed with 30% ground granulated blast furnace slag. It was intended to create a mortar using these kinds of cement to understand the compressive strength and some durability. And from the hydration reaction and product, we have also added to the discussion of the results.

2.1 Materials and mix proportions

Using Ordinary Portland cement does not contain the small amount of 5% components in the cement. As admixture was used fly ash (FA) which having a high salt attack resistance and limestone powder (LSP) which having the effect of promoting the reaction of cement and blast furnace slag. Table-1 shows the percentages of the binder were examined in this study. In this study, it was used to the cement was added limestone powder (LSP) and fly ash (FA) as admixture blast furnace slag cement type A (BA). It was prepared OPC, BA and BB also for comparison. Parameters were two systems. As the first one, it was constant at 30% the proportion of blast furnace slag in a binder. And, 5, 10, and 20% were varied with the ratio of the LSP and FA added to the OPC of the remaining 70%. Another it was constant at 70% of OPC in the proportion of binder. And, 5, 10, and 20% were varied with the amount of FA and LSP in the binder.

2.2 Testing methods

(1) Compressive strength

It was prepared the mortar on 50 % water-cement ratio. It was carried out in an environment sealed curing temperature of 20 degree Celsius, until the age of specimen compressive strength test were carried out at 3,7,28,91 days.

(2) Salt penetration test

Salt penetration test was carried out in the following manner. It was demolded in one day, the specimens were allowed to cure for 7 days sealed. Then, immersed in 3% salt concentration, we have measured salt penetration depth on 2, 4, 8 weeks by silver nitrate solutions.

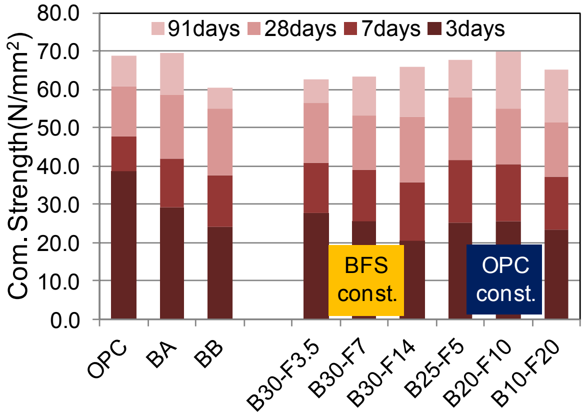

Figure-2 Result of Comp. Strength (effect of FA)

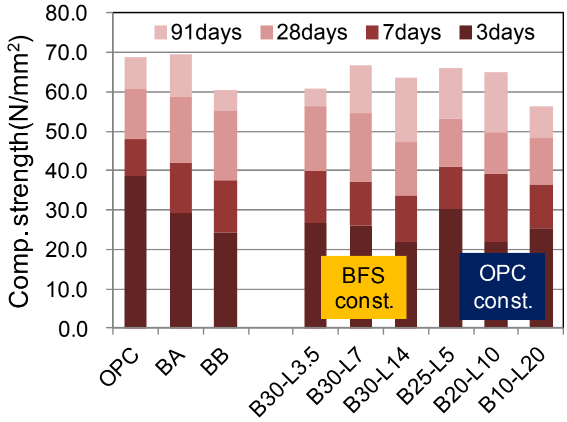

Figure-3 Result of Comp. Strength (effect of LSP)

(3) Accelerated carbonation test

Accelerated carbonation testing was performed in the following manner. Same salt attack test, it was demolded in one day, the specimens were allowed to cure for 7 days sealed. Then, constant temperature and humidity room (temperature 20 degree Celsius, relative humidity 60%) was allowed for 7 days. Then, it was allowed to accelerated carbonation environment, 5% carbon dioxide concentration, temperature 20 degrees Celsius, relative humidity 60%. We have measured carbonation depth on 2, 4, 8 weeks by phenolphthalein solutions.

(4) Accelerated ASR test

Specimens that remolded at one day were stored in the environment temperature of 40 degrees Celsius, relative humidity of 95%., The amount of expansion of the specimen was measured at 2,4,8,13 weeks, and we evaluated the resistance of ASR. It is to adjust the amount of alkali, alkali contained in the cement is only OPC. Specimens were prepared to the total alkali 1.2% adding the NaOH solution. Reactive aggregate was replaced by 50% in the fine aggregate.

3. Result of experiment

3.1 Compressive Strength test

(1) Effect for replacement of FA

Figure-2 shows the result of compressive strength. The compressive strength of age 3,7,28 days did not exceed that of OPC. However, at the age of 91 days, only the B20-F10 exceeds the compressive strength of the OPC.

In addition, with the increase of replacement ratio FA, increased growth in the strength of age from 28 to 91 days. This is considered to be the effect of pozzolanic reaction. However, due to significantly greater, increase the intensity of the B20-F10 did not reach in the B10-F20. This is true when there is a high rate of FA replacement, in the age of up to 91 days is not enough age for development of strength.
(2) Effect for replacement of LSP
Figure-3 shows the result of compressive strength. The case of a certain amount of BFS, it is increases of replacement ratio LSP, it is increases in growth of 91 days from the date of the strength of 28 days. This is probably because the LSP is to accelerate the reaction of BFS. Both the OPC in certain cases, the intensity of the 7, 28, 91 days was the result of decreases with increasing replacement percentage LSP.

3.2 Salt penetration test

Figure-4 shows the result of depth of salt penetration. Salt penetration depth of the mixed FA mortar is protected especially in any age than OPC. In addition, when compared with the results of 8 weeks, regardless of the degree of substitution of the FA, BFS certain formulation, the salt penetration depth is same. On the other hand, in certain cases OPC, due to the higher replacement of FA, there is a tendency for salt penetration depth increases. Also in the LSP mortar is mixed, the salt penetration depth showed a tendency similar to that of FA. From the above results, the salt penetration depth is greatly affected on content of BFS. Therefore, from the result of the combination of all mortar, we have investigated the relationship between the salt penetration depth and content of the BFS. The results are shown in the figure-5. From this figure, the BFS content increases, there is a tendency that the sat penetration depth is reduced. It was obtained the high correlation. If the binder is added BFS, so that the content of BFS is large, an increase in chloride ion fixed have been reported. Presumably had a major impact on the depth of salt penetration by chloride ion is incorporated into the hydration products. It is considered that the above-mentioned effect of FA is also observed, however, does not affect the outcome of this is unclear. We are going to continue to study in the future.

3.3 Accelerated Carbonation test

Figure-6 shows the result of accelerated carbonation test. First, we compared the carbonation depth of 8 weeks of mortar containing FA. Case of a certain amount of BFS, it was a result of carbonation depth increases the larger the amount of FA. Also, in the case of a certain amount of OPC, it was not observed the clear relationship. It was focused on the case of replacement of LSP. In certain mix proportion both with BFS and with OPC, it was increased the content of the LSP, resulted in carbonation depth increases. In general, due to an increase in the amount of binder powder added in an accelerated carbonation environment showed a tendency carbonation depth increases. This tendency is the same even when the

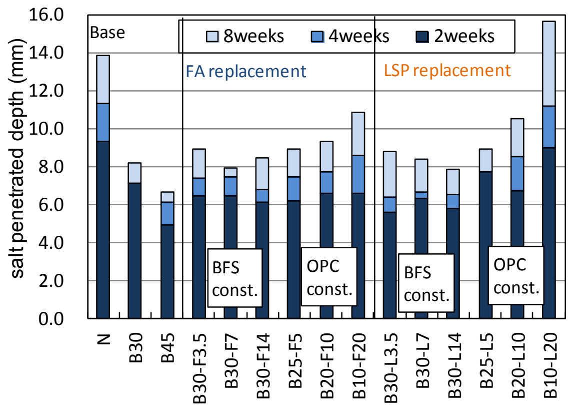

Figure-4 Result of salt penetration test

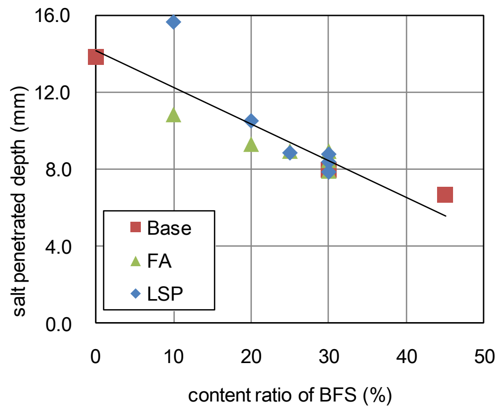

Figure-5 Relationship BFS content and salt resistance

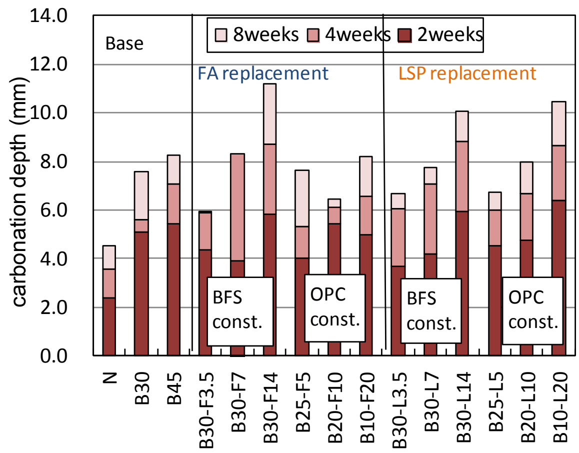

Figure-6 Result of carbonation test

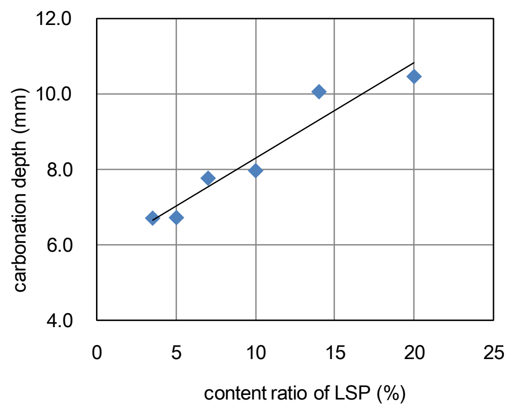

Figure-7 Relationship LSP content and carbonation

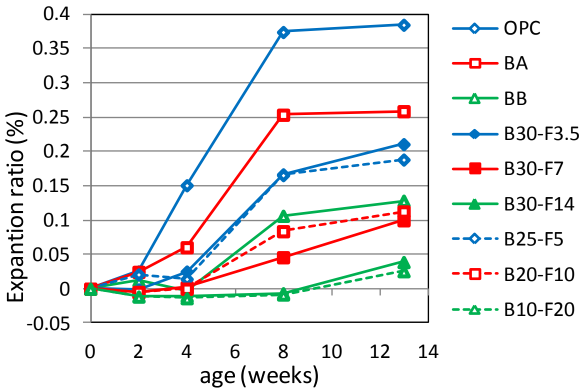

Figure-8 Expansion ratio of FA content cement

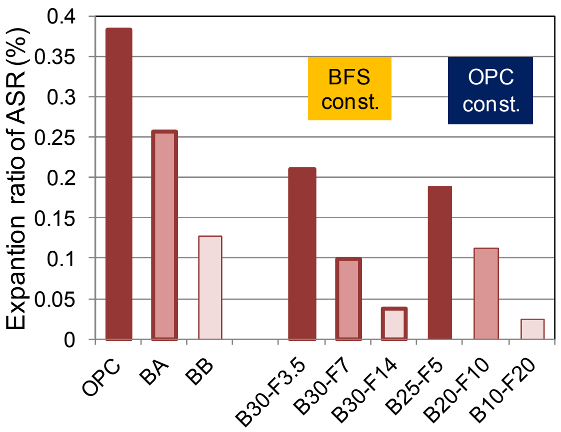

Figure-9 Expansion ratio of ASR at 13 weeks (FA)

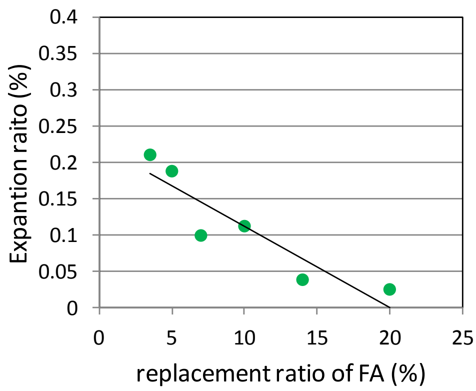

Figure-10 Relationship FA content and ASR resistance

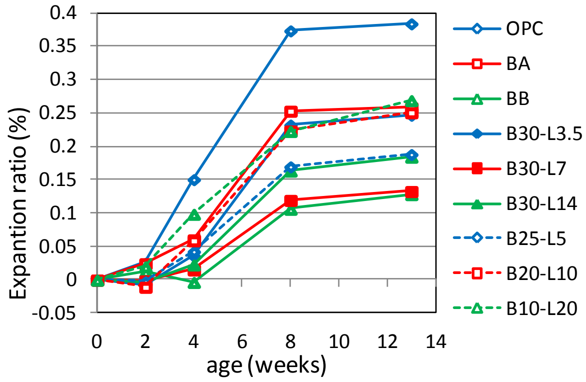

Figure-11 Expansion ratio of LSP content cement

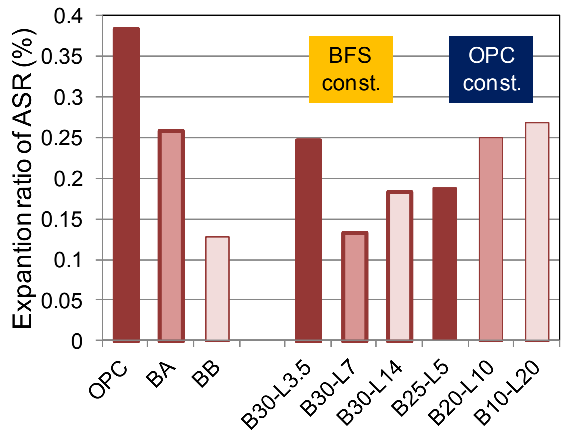

Figure-12 Expansion ratio of ASR at 13 weeks (LSP)

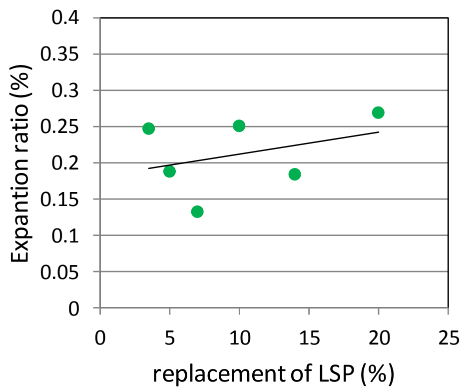

Figure-13 Relationship LSP and ASR resistance

base, replacement of FA and LSP, in certain cases only the OPC on replacement of FA, it was different. Figure-7 shows the relationship between the carbonation depth and the amount of addition LSP. It was found that the larger the carbonation depth of the LSP content increases.

3.4 Accelerated ASR test

(1) Effect for replacement of FA

Figure-8 shows the expansion ratio due to ASR and figure-9 shows comparing the expansion ratio on 13 weeks. With the increase in the added amount of FA, the expansion ratio is reduced. Therefore, figure-10 shows the relationship between the expansion rate at 13 weeks and the amount of FA in binder. It was observed the high correlation between the two. Therefore, I find that FA has a high inhibitory effect against ASR. The reason for this is to be considered, Environmental conditions in the accelerated ASR test conditions, such as temperature 40 degrees Celsius, 95% relative humidity, pozzolanic reaction proceeds well in the 13 weeks. It may be due to the fact that the $Ca(OH)_2$ is used in the cement harden, the alkali is reduced. Future, we are going to make the determination of calcium hydroxide using a TG-DTA, to verify the correlation between resistances to ASR.

(2) Effect for replacement of LSP

Figure-11 shows the expansion ratio due to ASR and figure-12 shows comparing the expansion ratio on 13 weeks using LSP. Inhibitory effect of B30-L7 is about the same as observed in BB. However, in the other cement resulted in expanding than BB. In case of certain OPC, with increasing content of the LSP, the

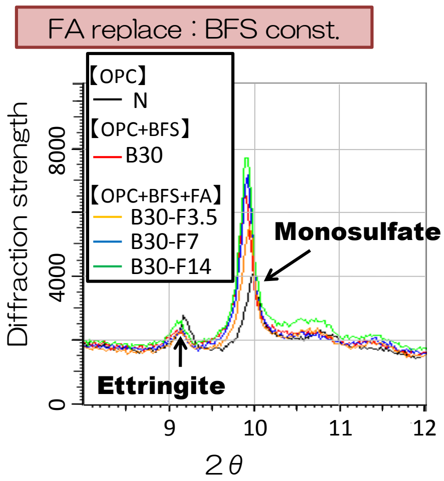

Figure-14 Cement hydrate products of FA replacement

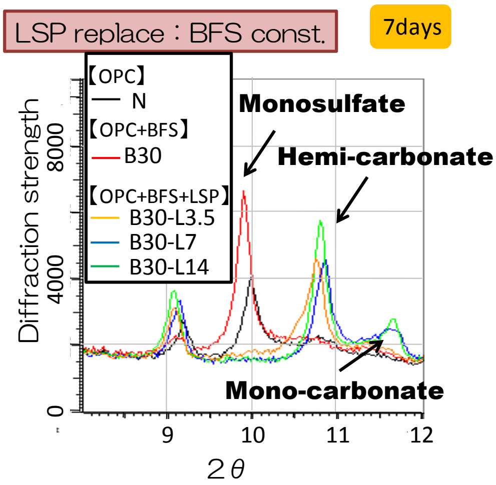

Figure-15 Cement hydrate products of LSP replacement

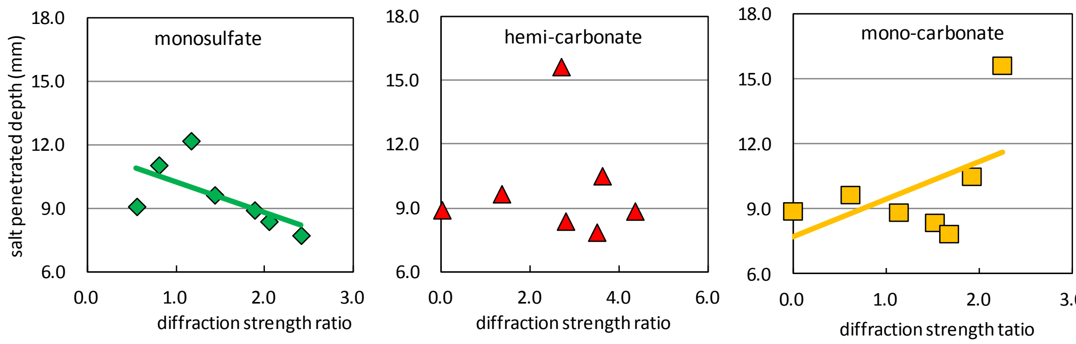

Figure-16 Relationship cement hydration product and salt resistance

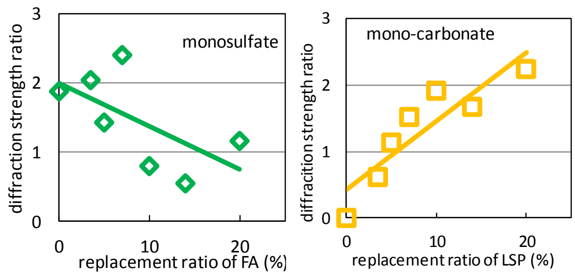

Figure-17 Relationship FA, LSP and cement hydrate

expansion ratio is increased. Figure-13 shows the relationship between the expansion rate and the content of the LSP as well as FA. From this, it is considered that LSP doesn't have the resistance of ASR.

4. Discussions

4.1 Outline of quantitative hydration product

Considering the results of this study, on carbonation, ASR and compressive strength, the arrangement was possible due to the content of the various binders. However, it is not clear that the relationship on salt penetration. In this paper we examine the hydration products of each used binders. In addition, we also examine the products after the salt penetration. Methods for determination of product were assumed by XRD on cement paste samples. As cement hydrates, we were targeting ettringite, monosulfate and carbonate hydrate systems. In addition, as the salt product after the salt penetration, we were focusing on Friedel's salt.

4.2 Result of XRD

Figure-14 and Figure-15 show the result of XRD on FA content and LSP content at 7 days. Hydration product is found to be identical to OPC and B30. Hydration products were ettringite and monosulfate. It was also to be the same with the product containing the FA, the amount of the product is different. On the other hand, the case of containing LSP, it was generating the different type of hydrate products with OPC. It was not generated the monosulfate, there is the mono-carbonate and hemi-carbonate hydrate such as carbonate hydrate.

Here, figure-16 shows the relationship between the generated hydrate amount (such as monosulfate, hemi-carbonate and mono-carbonate) and the depth of salt penetration. The amount of hydrate has the diffraction peak intensity ratio. On the monosulfate, it was observed that the diffraction peak intensity ratio increases, the salt penetration depth decreases. On the hemi-carbonate, it was not cleared the relationship between the two. On mono-carbonate, it was observed that the diffraction peak intensity is large the salt penetration depth is also larger. Figure-17 shows the relationship between the amounts of FA content and generated monosulfate products. Therefore, the amount of production of monosulfate is highly correlated with the content of FA. For this reason, salt penetration has been suppressed by mixing FA. On the other hand, Figure-17 shows the relationship between the amounts of LSP and mono-carbonate products. It can be inferred mono-carbonate generated by the addition of LSP, salt

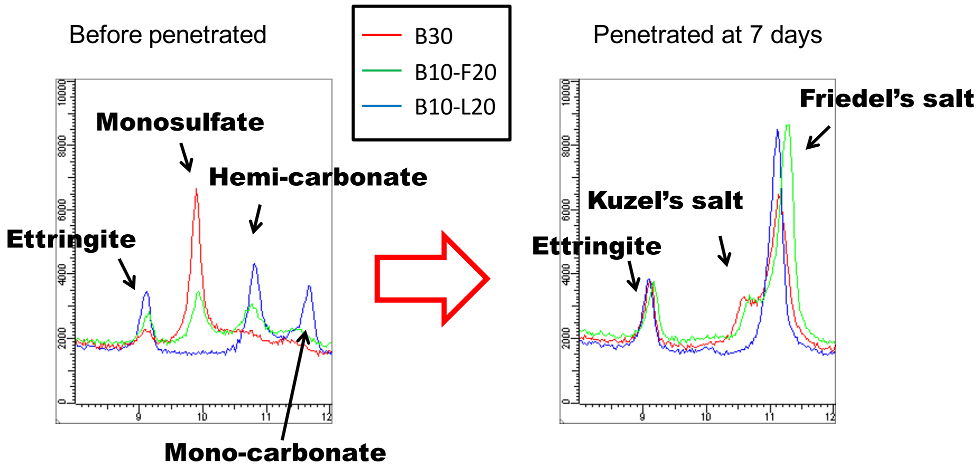

Figure-18 hydrate products after salt penetrated at 7 days

penetration increases.

Finally, Figure-18 shows the difference of products between before and after the salt penetration. Before salt penetration, it is similar to the FA containing cement paste and the B30 as described above. However the LSP containing samples can be confirmed carbonate-based hydrate system. After 7 days on salt penetrating, we were able to confirm Friedel's salt and ettringite in all samples. And it can be confirmed the Kuzel's salt in the FA and B30, however we could not be confirmed in the LSP. It is believed that to have a significant impact on salt penetration, it is necessary to proceed with further studies in the future.

5. Calculation of CO_2 emissions

It was tried to calculate the CO_2 emissions of cement used in this study using inventory data. Table-2 shows the inventory data for CO_2 emissions on those materials. Table-3 shows the result of calculation of CO_2 emissions and reduced ratio as OPC. Basically, there is a correlation between the amount of CO_2 emissions and high content OPC. Therefore, it is difficult to reduce the amount of CO_2 emissions in the extreme. However, because it can be reduced more than 30% compared with OPC, if OPC was used as a substitute for, we can expect the effect of CO_2 reduction.

Table-2 Inventory data of CO_2 emissions

material	OPC	BFS	FA	LSP
CO2 emission (kg-CO2/t)	757.9	24.1	17.9	16.1

Table-3 CO_2 emissions of cement on this research

			CO2 emissions (kg/t)	reduce ratio (%)
OPC 100%		OPC	758	-
BFS 30%		BA	538	29.0
BFS 45%		BB	428	43.6
FA replace	BFS constant	B30-F3.5	512	32.5
		B30-F7	486	35.9
		B30-F14	434	42.7
	OPC constant	B25-F5	537	29.1
		B20-F10	537	29.1
		B10-F20	537	29.1
LSP replace	BFS constant	B30-L3.5	512	32.5
		B30-L7	486	35.9
		B30-L14	434	42.7
	OPC constant	B25-L5	537	29.1
		B20-L10	537	29.1
		B10-L20	537	29.1

6. CONCLUSIONS

The following are the results in this study.

(1) As the cement content increases FA, an increase in growth of 91 days from 28 days on the compressive strength. Enhancement of long-term strength can be expected. Cement was added to the LSP, the promotion of long-term strength cannot be expected.

(2) Within the scope of this study, on salt penetration depth, the effect of BFS is greater than LSP and FA in the cement containing the LSP and FA. In other words, the higher the content of BFS, and high resistance to salt penetration.

(3) In salt penetration, it is possible to suppress the generation of monosulfate. On the other hand, we found that salt penetration resistance is reduced in production of mono-carbonate. Therefore different product was confirmed by FA and LSP after salt penetration.

(4) In the carbonation test, the higher the content of the LSP, carbonation depth increases.

(5) On inhibitory effect on the ASR, FA high inhibitory effect is observed, but, LSP was not observed.

(6) Within the scope of this study, mix proportion as B20-F10 has the compressive strength of the same degree of OPC at 91 days, and also has ASR inhibitory on BB. In this way, it has suggested the possibility of new mixed cement can be manufactured in accordance with the required performance.

REFERENCES

1. Y. Takahashi, H Murakami and T Iyoda: properties strength and ASR resistance on different cement type, JSCE kanto, Vol.39, V-38, 2012 (*In Japanese*)