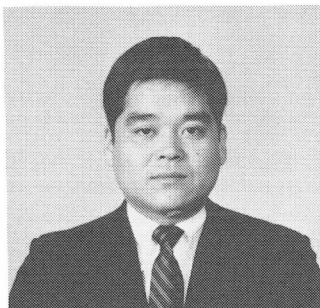
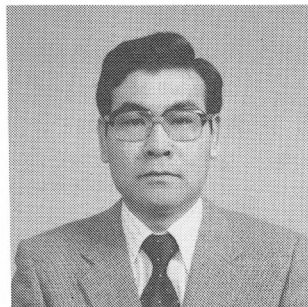


UTILIZATION OF FERRO-NICKEL SLAG AS FINE AGGREGATE FOR CONCRETE

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SYNOPSIS

A total of eight ferro-nickel slags were studied for their possibility of being used as fine aggregate in concrete. Special emphases were placed on their effects on the freeze-thaw resistance and long-term stability of concrete. It was observed that the freeze-thaw resistance of slag concrete was generally lower than that of ordinary concrete with river sand. The increased bleeding of slag concrete was mainly responsible for the low freeze-thaw resistance. Slags which were composed of only forsterite and amorphous silica were found to cause a reaction with alkalis in concrete, while other rapidly but rather moderately-cooled slags were stable. Grain popouts were observed when certain slags were used. Three slags were considered not to impair the durability of concrete. Properties of fresh concrete were also discussed briefly.

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1. INTRODUCTION

A total of two million tons per year of ferro-nickel slags (hereafter, they will be referred to simply as slags) are discharged as a by-product from the furnaces for ferro-nickel production in Japan. They are usually water- or air-granulated to the sizes of sand during their drawing from the furnaces. About 30 percent of the slags are utilized as a raw material in the production of iron, fertilizers and others, while the majority of the rest are not effectively utilized; most of them are used only as a filling material for reclaimed land and the subgrade of roads. According to the recent report [1] of preliminary studies on the qualities of the slags available in Japan, the slags possess satisfactory physical properties for concrete aggregate, and neither dusting nor mineral transformation of slag particles occurs during their long time storage. If these are the cases, the slags should be studied further for their possibility of being used as fine aggregate for concrete not only in view of the effective utilization of resources and/or byproducts but also considering the recent shortage of natural aggregate with good quality in Japan.

Only a few studies have been made on the use of this kind of slags as fine aggregate for concrete before 1980. The study reported in 1965 by Shirayama [2], in which he recommended to use the slag by combining it with river sand to improve its poor grading, would be the first work on the subject. Another extended study was made by Hasaba et al. reporting in 1976 that the slag they studied possessed a high alkali reactivity [3]. However, all the papers reported before 1982 dealt with only one kind of slag produced through a particular process. In 1982, Japan Mining Industry Association (JMIA) entrusted both Japan Society of Civil Engineers (JSCE) and Architectural Institute of Japan (AIJ) with the research work on the use of slags in concrete. Approximately 4 to 5 valuable studies on the slags have been published annually [4]-[13] since then, and general characteristics of the slags as fine aggregate for concrete have been disclosed gradually through these works. However, little information is available on the proper mix proportions of slag concrete and properties of unhardened slag concrete. The freeze-thaw resistance of slag concrete and the stability of slag particles in concrete are other important aspects which have been examined to some extent by other workers but require further intensive study.

The present paper discusses the results of tests conducted to examine the feasibility of using the slags as fine aggregate for concrete. All the eight kinds of slags obtainable in Japan were included in the tests. Special emphases were placed on their effects on the freeze-thaw resistance of concrete and the long-term stability of slags in concrete. The results of previous studies by the authors [11]-[13] on the optimum sand-aggregate ratio, properties of fresh concrete, and other related properties were further examined.

2. MATERIALS

The physical properties of the slags are shown in Table 1 together with the types of furnace from which they were drawn and cooling procedures at their drawing time. As seen in the table, the slags can be classified into 3 kinds depending on the types of furnace, and also 3 depending on the cooling procedures. For some slags, two values are shown for each quantity in Table 1. The values in the upper line are those of the slags used in the tests in Chaps. 3 and 4, or for concretes prepared in Chap. 6. Those in the lower line are for the slags used in the tests in Chap. 5, for the preparation of mortar specimens in Chap. 6 and in some tests in Chap. 4 that were made to study the air entrapping in slag concrete and combined use of slags with river sand.

The slags are mainly composed of SiO_2 and MgO as shown in Table 2. The particles of water-granulated slags and air-cooled slag are mostly angular and rough, because they are usually subjected to crushing in their manufacturing process. Air-granulated slag, on the other hand, is mainly consisted of spherical particles with smooth texture. All the slags were used in concrete after conditioning their moisture contents so as to contain about 1% surface water.

For the purposes of comparison or combined use with the slags, Kinu river sand was used, whose physical properties are included in Table 1. Coarse aggregate used was crushed cobble stone taken from Kinu river with a maximum size of 25mm, specific gravity of 2.60, absorption of 1.30%, dry-rodded bulk density of 58.8%, and fineness modulus of 7.19. It was used in the water-saturated surface dry condition.

Table 1 Physical properties of slags and river sand.

FERRO-NICKEL SLAG			SPECIFIC GRAVITY	ABSORP-TION %	SOLID VOLUME PERCENTAGE %	SOUND-NESS LOSS %	GRADING							
NAME	TYPE	FURNACE					F.M.	PASSING PERCENTAGE , %						
								5mm	2.5	1.2	0.6	0.3	0.15	
S1	AIR-COOLED	ELECTRIC FURNACE	3.06	1.82	58.1	--	2.03	100	94	82	57	38	26	
S2**	AIR-GRANULATED		3.06	1.37	66.7	--	2.64	100	98	81	41	13	3	
S2'	AIR-GRANULATED		2.94	0.85	--	1.55	2.45	100	98	85	48	19	4	
S2'	AIR-COOLED		2.99	2.72	--	15.85	1.90	100	90	78	62	46	34	
S3	WATER-GRANULATED	ELECTRIC FURNACE	2.85	0.84	67.5	4.20	2.49	100	89	81	51	27	11	
S4			ROTARY KILN	3.09	0.75	61.5	--	2.56	100	93	70	47	25	9
S4				3.05	0.99	--	1.56	2.73	100	95	74	43	13	2
S5			BLAST FURNACE	2.71	1.53	57.2	--	2.62	100	95	77	44	16	7
S5		2.74		1.35	--	1.87	2.46	100	94	78	49	31	9	
S6		ELECTRIC FURNACE	2.85	1.13	66.7	--	2.66	100	94	75	52	21	3	
S6			2.86	0.91	--	2.77	2.43	100	95	79	47	29	13	
S7			3.00	0.96	67.0	--	2.74	100	100	79	31	13	4	
S7			2.95	1.12	--	1.88	2.31	100	100	94	46	19	10	
RIVER SAND			2.59	2.27	64.0	4.30	2.71	100	87	72	48	18	5	

* WATER-SATURATED SURFACE DRY CONDITION.

** S2 AND S2' WERE PRODUCED FROM THE MOLTEN SLAGS DRAWN FROM THE SAME FURNACE.

Table 2 Chemical compositions of slags.

SLAG	CHEMICAL COMPOSITION, %										
	SiO_2	MgO	CaO	Al_2O_3	FeO	Cr	Ni	Mn	S	Na_2O	K
S 1	56.4	35.0	1.5	2.0	4.6	0.5	0.1	0.15	-	-	-
S2, S2'	53.2	34.4	1.5	2.9	6.2	1.0	0.04	0.18	0.03	0.0	0.0
S 3	56.0	36.5	0.8	1.5	5.4	0.1	0.07	0.03	-	0.24	0.05
S 4	54.1	28.4	5.5	2.4	7.7	0.8	0.3	0.2	0.04	0.05	0.05
S 5	50.6	26.0	14.3	3.7	4.4	0.3	0.06	0.21	0.21	0.0	0.0
S 6	54.2	37.0	0.2	1.2	6.4	0.5	0.07	0.22	0.03	0.0	0.0
S 7	52.2	33.7	0.9	1.5	9.0	0.8	0.06	0.33	0.02	0.04	0.04

Table 3 Properties of cements.

CEMENT	SPECIFIC GRAVITY	SPECIFIC SURFACE (CM ² /G)	SETTING TIME		STRENGTH (MPa)						CHEMICAL COMPOSITION, %					
			INITIAL (HR-MIN)	FINAL (HR-MIN)	FLEXUAL			COMPRESSIVE			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
					3D	7D	28D	3D	7D	28D						
CEMENT 1	3.16	3260	2-35	3-37	3.3	4.8	6.9	13.6	22.7	40.3	22.0	5.4	3.1	65.1	1.3	1.8
CEMENT 2	3.16	3210	2-32	3-38	3.4	4.8	7.0	13.9	22.7	40.3	22.2	5.4	3.1	65.1	1.2	1.9

Table 4 Optimum sand-aggregate ratio (%) of concrete*.

TEST METHOD	FINE AGGREGATE							RIVER SAND
	S1	S2	S3	S4	S5	S6	S7	
CONSISTOMETER	35	43	43	40	39	40	43	43
TRIAL MIXING	33	43	43	40	39	40	43	43

* PLAIN CONCRETE : W/C = 60% , SLUMP = 8CM.

Two portland cements conforming to ASTM Type I were used. Their physical and chemical properties are given in Table 3. Cement 2 was used only in those parts of the studies where the freeze-thaw resistance of concrete, effect of combined use of slags with river sand in concrete and alkali-silica reactivity of slags were examined. The alkali content of cement 2 was 0.66% in Na₂O equivalence. Vinsol(resin type) was used as an air-entraining admixture.

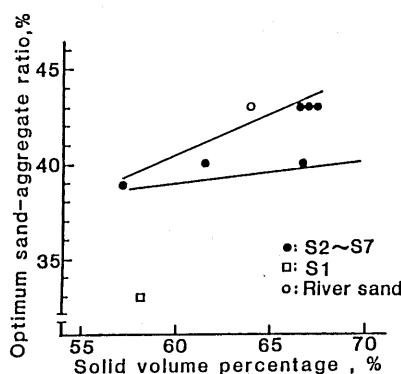


Fig.1 Solid volume percentage of sand vs. optimum sand-aggregate ratio.

3. PROPORTIONING OF CONCRETE MIXES MADE WITH SLAG

Since the slag particles were peculiar in their shapes and surface textures as mentioned before, the effects of these peculiarities on the mix proportions of concrete were studied with special emphases placed on their effects on sand-aggregate ratio and water requirement.

First of all, optimum sand-aggregate ratios were tested by usual method using a vibrating consistometer [11], and, then, the results were further confirmed or modified through trial mixing. Table 4 summarizes the results obtained from each of these two methods for plain concretes with 60% water-cement ratio and 8cm slump. As seen in Table 4, the method by the consistometer gave about 2% higher value than the most desirable one only in the case of concrete with S1 (air-cooled slag).

It is seen in Table 4 that the optimum sand-aggregate ratios for all the slags except S1 are nearly equal to or a little lower than the ratio for river sand. In order to investigate the reasons for this trend, the solid volume percentages of slags of the same gradings as those used in concrete were measured and the results were plotted against their optimum sand-aggregate ratios in Fig. 1. The tendency observable in Fig. 1 is considered to indicate that sand-aggregate ratio should be lowered as the angularity of sand particles is increased. This result is in contradiction to the general belief that sand-aggregate ratio must be increased when crushed fine aggregate is used[14][15]. However, it should be mentioned here that the workability of concrete would be improved as the influence of undesirable factors, i.e., angularity of aggregate, is lessened. This concept would suggest that when angular fine aggregate is used, it is considered to be adequate to decrease the sand-aggregate ratio of concrete as was shown in the present study, or to increase the volume of finer materials than fine aggregate such as cement and/or mineral admixtures.

The optimum sand-aggregate ratio for S1 was quite small mainly because its grading was finer than that of others and it contained a considerable amount of fine powders. These characteristics of S1 may be responsible for its isolated data point in Fig. 1.

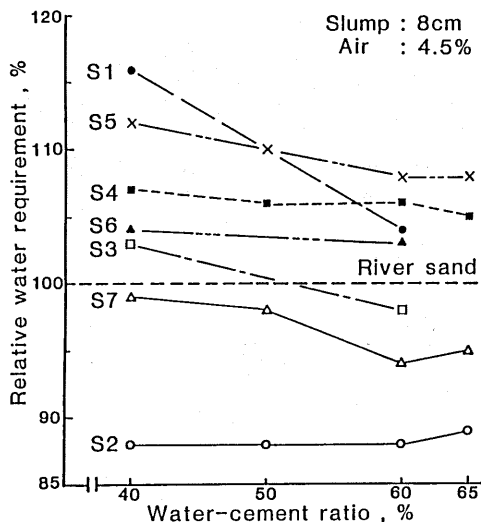


Fig. 2 Water-cement ratio vs. water requirement.

Fig. 2 shows the relationship between water-cement ratio and water requirement for obtaining concrete with 8cm slump and 4.5% air content. The water requirements in Fig. 2 were expressed in percentages of the water requirements of slag concretes to those of corresponding river-sand concrete. A noteworthy result in Fig. 2 is that concretes with S2, whose particles were mostly spherical, required more than 10% less water than those with river sand. On the contrary, the use of other crushed slags generally increased the water requirement by about 15% at maximum, although the extent of which became smaller as water-cement ratio was increased. S3 and S7 decreased or increased the water requirement only a little regardless of their angular shapes.

Figure 3 shows the relations between the water requirements in Fig. 2 and solid volume percentages of the slags, plotted for the cases of water-cement ratios of 40 and 60%. It is seen in the figure that the slags of larger solid volume percentage required less water as usually seen in the case of coarse aggregate. This trend in Fig. 3 would indicate that the differences in the water requirement among the slags observable in Fig. 2 were mainly caused by the differences in their particle shape. It may be added that the data points of S2 were located below the relations for the other slags in Fig. 3, presumably indicating that the spherical shape and smooth surface of S2 particles contributed extraordinarily to the reduction of water requirement.

The required dosages of air-entraining admixture to provide a prescribed amount of air in concrete were nearly equal to those of concretes with river sand when water-granulated slags or air-granulated slag were used (See Fig. 4). However,

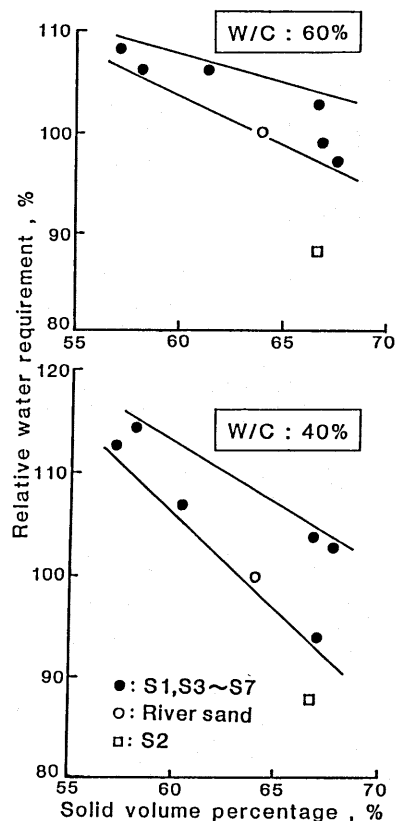


Fig. 3 Solid volume percentage of sand vs. water requirement.

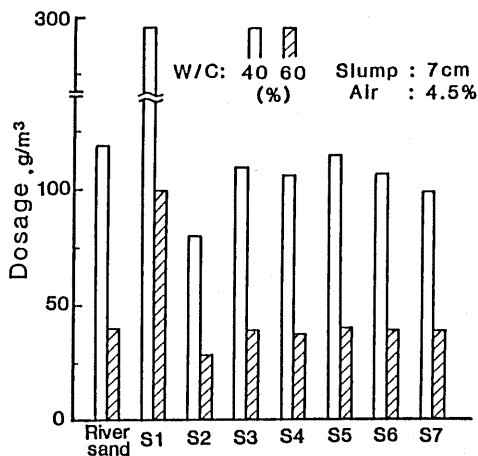


Fig. 4 Required dosage of air-entraining agent.

air-cooled slag (S1) required two to three times more air-entraining admixture than the others. The reason for the latter result may be that the large amount of fines in S1 played a similar role to that of cement in rich mix concrete.

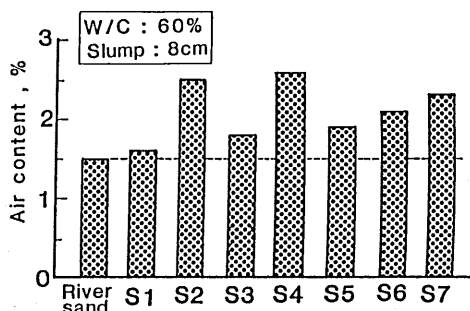


Fig. 5 Air content of plain concrete.

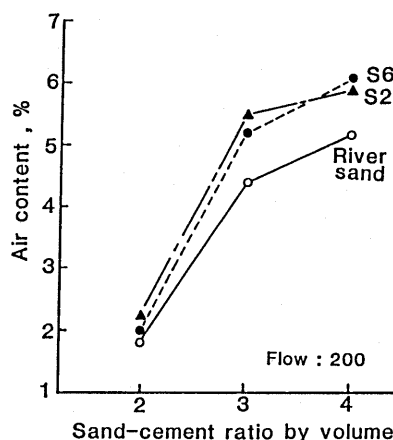


Fig. 6 Air content of plain mortar.

4. PROPERTIES AT FRESH STAGE AND COMPRESSIVE STRENGTH OF SLAG CONCRETE

It is known that a relatively large amount of air is entrapped in plain concrete when water-granulated blast furnace iron slags are used as fine aggregate, while air-granulated slags do not possess such a peculiarity [14]. In the cases of the slags under the present study, a considerable increase in entrapped air was observed when both types of slags were used; the air-granulated type (S2) also entrapped about 1% higher air in concrete compared with river sand (See Fig. 5). Kobayashi et al. observed a similar increase in the entrapped air with the slags and attributed it to their high contents of 0.6 to 1.2mm size grains [9]. However, using the air-granulated slag (S2) or water-granulated slag (S6) whose grading was exactly the same as that of river sand still entrapped approximately 1 percent higher air in mortar compared with the case of using river sand (See Fig. 6). In addition, a close examination of the relation between the gradings of the slags used in the test for Fig. 5 and the amount of entrapped air revealed that no such correlation as suggested by Kobayashi et al. existed.

It was expected at the first that one of the reasons for the increased air in concrete with air-granulated slag (S2) was due to its about 10% lower cement requirement than the case with river sand when both the water-cement ratio and slump were kept constant. However, it was found in another series of test that

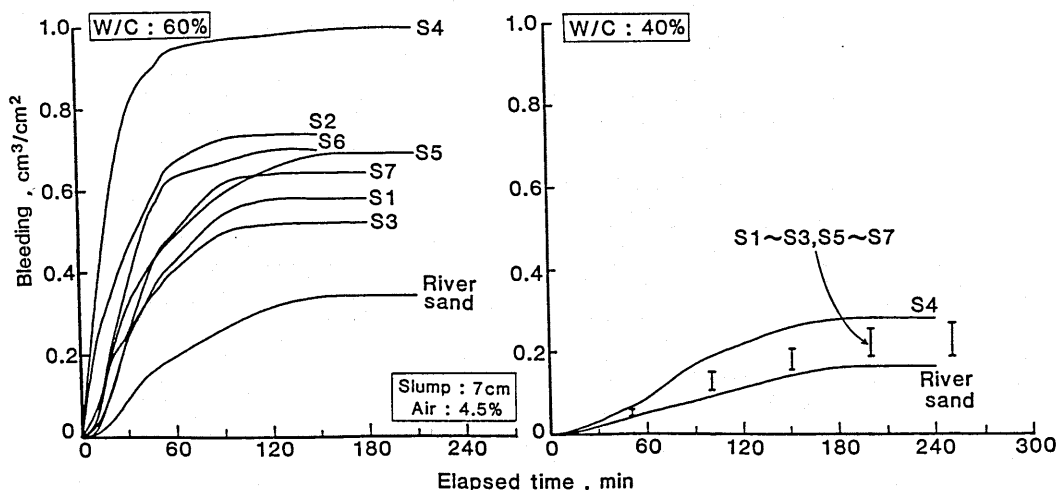


Fig.7 Test results of bleeding.

the air contents of three concretes, whose cement contents were set at 250, 300 and 350 kg/m³ holding their slump at 8 cm, were 4.2, 3.6 and 3.1%, respectively, indicating that 10% reduction in cement was responsible only for about 0.3% increase in air. Thus, the reasons for the large amount of entrapped air in slag concretes could not be fully clarified. Whatever the reasons are, however, this effect must be counted in selecting the air content of concrete, especially when high freeze-thaw resistance of concrete is required.

The use of slags generally increased the bleeding of concrete; the tendency becoming more notable in leaner mixes (See Fig.7). This may be due to the inherent properties of slag particles, i.e., large specific gravity and poor water retentivity due to their smooth surface, as in the case of granulated blast furnace iron slags. The blended use of slags with river sand was effective to reduce the bleeding of slag concretes (Fig. 8).

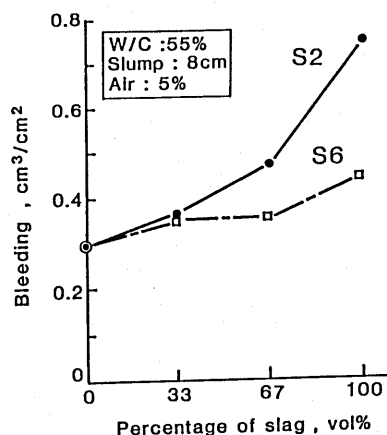


Fig.8 Volume percentage of slag vs. bleeding.

The setting time of slag concrete was nearly equal to that of ordinary concrete with river sand (Fig. 9).

The relation between compressive strength and cement-water ratio was examined for slag concrete at the ages of 3, 7 and 28 days and at 6 months. One air-granulated slag (S2) and three water-granulated slags (S4, S5, S7) were used in this series of test. Cylindrical concrete specimens of 100mm in diameter and 200mm in height, which were demolded at 2 days and subsequently cured under water at 20 C, were used for the test. Uomoto and Hoshino [8] reported that

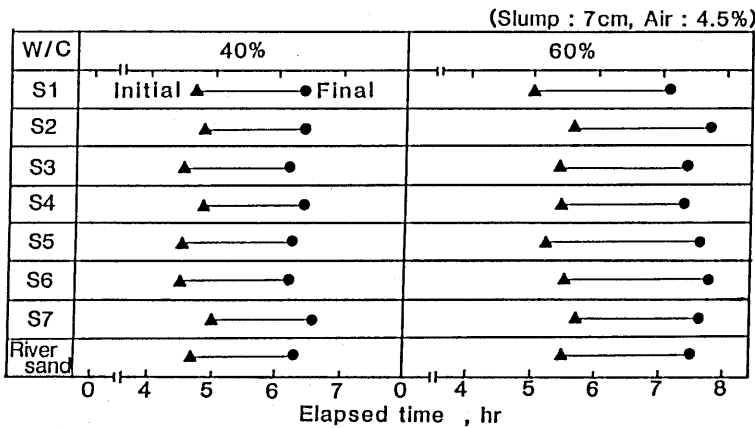


Fig.9 Test results of setting time.

both the flexural strength and tensile strength of slag concrete were comparable to those of ordinary concrete, while its compressive strength was a little lower. The latter trend can be seen also in Fig. 10 which shows the results of the present study. However, the strength reduction of slag concrete observable in Fig. 10 is not so significant. Therefore, no special precautions will be required in using the slags as far as their effects on the strength of concrete are concerned.

Since most of the slags are produced by rapidly chilling the molten slags, it was expected that they might possess a latent hydraulicity similar to that of granulated blast furnace iron slags. In order to examine this property, all the slags were kept immersed in a saturated water solution of $\text{Ca}(\text{OH})_2$ for about one year. However, no apparent agglomeration or cohesion of slag particles was observed, indicating that they possessed little latent hydraulicity. The similar rate of increase in the strength of slag concrete to that of river-sand concrete at later ages observable in Fig. 10 would be due to the negligible latent hydraulicity of the slags.

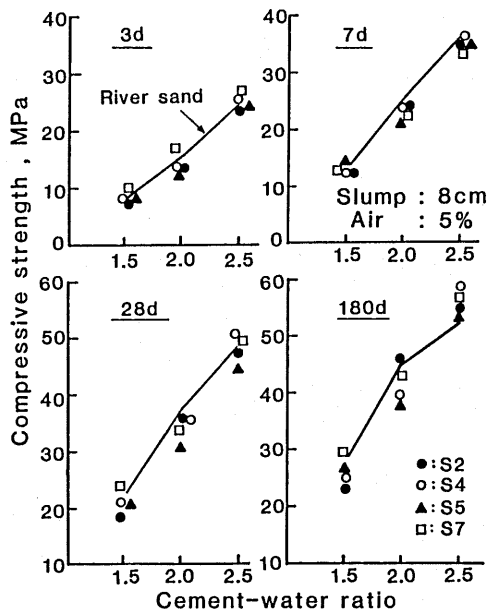


Fig.10 Test results of compressive strength.

5. FREEZE-THAW RESISTANCE OF SLAG CONCRETE

Freeze-thaw resistance was tested for concretes made with 4 kinds of slags whose types of furnace and cooling procedures were different one another. Water-cement ratio and slump were kept at 55% and 8cm, respectively. Three to six levels of

air content were selected for each slag in the range of 3 to 9%. The test was conducted in accordance with the method described in the annex of JIS A 6204 except that 300 cycles of freezing and thawing were preformed. This method is similar to ASTM C 666 Procedure A.

Fig. 11 shows the test results expressed in the relation between air content and durability factor. Kobayashi et al. [9] reported that the frost resistance of slag concrete was generally lower than that of ordinary concrete at a fixed air content, and that of concrete with air-granulated slag (S2) was particularly low. These trends can be also seen in Fig. 11. However, it should be noted in the figure that the freeze-thaw resistance of concrete with S4 was also extremely low and was not improved at all even when the air content was increased. Since the characteristics of slag particles themselves and/or slag concretes are considered to be responsible for the poor freeze-thaw resistance, these effects were examined next.

It is generally believed that, as far as the properties of aggregate are concerned, its strength and pore system (volume and size of pores) are two main factors which have considerable influence on the freeze-thaw resistance of concrete [16]. However, judging from the results of soundness test in Table 1, the effects of the former is considered to be little in the cases of the slags under the present study. Hence, pore systems of the slags used in the test of Fig. 11 were examined next by mercury pressure porosimeter for particles of 1.2 to 2.5mm size.

Fig.12 shows pore-size distribution obtained by assuming that the surface tension and contact angle of mercury are 480 dyn/cm and 141.3 degrees, respectively. Values of total pore volume (T.P.V.) measured at 1000 kgf/cm² (98MPa) are also shown in the figure. The comparison of these results with those in Fig. 11 would reveal no consistent

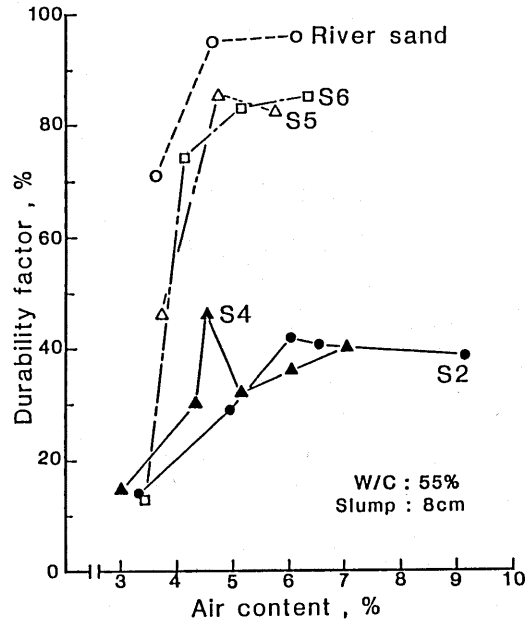


Fig.11 Air content vs. durability factor.

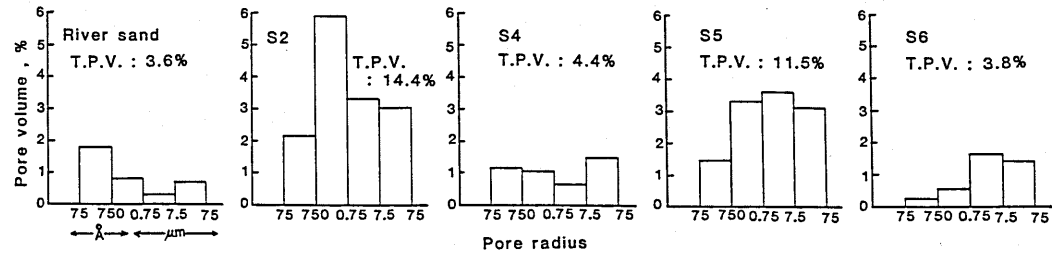


Fig.12 Pore-size distribution and total pore volume of fine aggregate.

relations between the pore-size distribution or total pore volume of slag particles and the freeze-thaw resistance of slag concrete. Therefore, it is conceivable that the poor freeze-thaw resistance of slag concrete was caused by other factors; i.e., the characteristics of slag concrete.

In the preceding chapters, the followings were shown as general characteristics of slag concrete.

(A) Increased entrapped air in concrete

(B) Increased bleeding

(C) High water requirement except for the case with air-grauulated slag

All of these characteristics can be factors to cause the reduction of freeze-thaw resistance of moderately air-entrained concrete. However, the effect of (A) will not be the main cause in the case of the present study, because the freeze-thaw resistance could not be improved at all even when air was increased to considerably high level (See Fig. 11). Nor will be the effect of (C) because concretes with air-granulated slag (S2) which required about 10% less water than river sand also possessed a poor freeze-thaw resistance, although high water requirement often results in increased bleeding. Therefore, the relation between the rest of the characteristic, i.e., (B), and freeze-thaw resistance was investigated next.

According to the results of bleeding test in Fig. 7 for the case of water-cement ratio of 60%, which is not so different from the water-cement ratio employed in the freeze-thaw test, the amount of bleeding of concrete with S2, S4, S5 or S6 is more than twice that with river sand. The larger the amount of bleeding water, the more the water channels of bleeding in concrete and water cavities beneath aggregate particles. The existence of these defects will impair the freeze-thaw resistance of concrete. Therefore, it is conceivable that the increased bleeding of slag concretes was responsible for their poor freeze-thaw resistance. The extremely low freeze-thaw resistance of concrete with S4 may be explained by its remarkably increased bleeding. However, the quite low freeze-thaw resistance of the concrete with S2 will still remain unexplained because the bleeding of concrete with S2 was nearly same as that with S5 or S6.

Since bleeding can be greatly reduced by lowering water-cement ratio or increasing cement content as seen Fig. 7, the effect of bleeding on the freeze-thaw resistance was further examined for the case with S2 by increasing the cement content to 400 kg/m³. Air content was changed into 3 levels in the range of 5 to 8%, and slump kept at 8cm. The test results indicated that the freeze-thaw resistance of concretes were improved significantly; the durability factors at 300 cycles of freezing and thawing exceeding 95% for all the specimens. Since their water-cement ratios were also lowered to 36 to 38%, a part of the reasons for the improved durability may be attributed to the increased strength of concrete and/or decreased volume of capillary pores. These effects, however, are known to be relatively small in the range of such water-cement ratios as those employed in the test [17] and, therefore, the improved freeze-thaw resistance of concrete with S2 is considered to have been brought by the reduced bleeding. This result would lead to the conclusion that it is important to reduce the bleeding of concrete to the lowest possible level by proper means in addition to sufficient air-entrainment when slag concretes are required to possess a high freeze-thaw resistance.

6. LONG-TERM STABILITY OF SLAG CONCRETE

The slags used in the present study are mainly composed of SiO₂ and MgO as mentioned previously. Since all the slags except S1 are chilled rapidly during their production, most of their SiO₂ may exist in a glassy or unstable state.

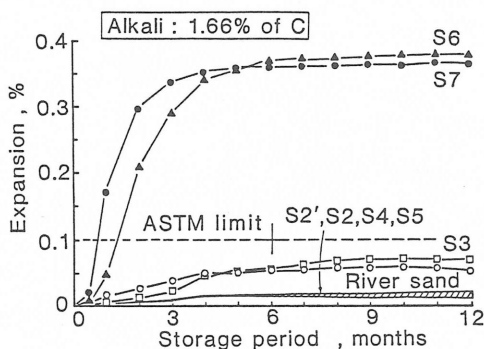


Fig.13 Results of mortar-bar test (NaOH added).

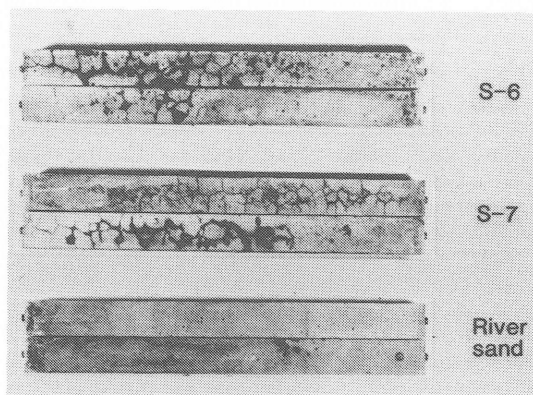


Photo 1 Map cracking of mortar.

If this is the case, they may cause alkali-silica reaction in concrete. On the other hand, if MgO exists in its free form, it may react with water to form $Mg(OH)_2$, causing an undesirable expansion in concrete. These reactivities of slags were studied in this Chapter.

(1) Alkali-Silica Reactivity of Slags

Fig. 13 shows the results of mortar-bar test conducted for 1 year to examine the alkali-silica reactivity of slags. The test was made in accordance with ASTM C 227 except that reagent grade NaOH was added in mixing water so that the total alkali content in mortar was 1.66% of cement by weight in Na_2O equivalence. According to Fig. 13, the expansions of mortars with S2', S2, S3, S4 and S5 are less than the ASTM limit (0.1% in 6 months). It should be noted that, when S2', S2, S4 and S5 were used, the resulted expansions were much smaller than that of river sand mortar, indicating that these four slags have little possibility of causing alkali-silica reaction in concrete. The reactivity of S3 is higher than that of the four innocuous slags but is considered to be very weak.

On the other hand, S6 and S7 caused about 3 times higher expansion of mortar than the ASTM limit in 3 months. Map cracks as shown in Photo 1 were observed to occur in the surface of the mortars when their expansions exceeded 0.1% at about 1 month of storage. These results would indicate that alkali-silica reactions occurred in the mortar with S6 or S7. Since it was expected that such unusual expansions were brought by the extremely increased alkali content in mortar, their alkali-silica reactivities were further tested in mortar with no alkali added. The innocuous S2 was also used in this test for a comparative purpose.

As seen in Fig. 14, the mortar with S2 showed a much smaller expansion than that in the previous test, and it was confirmed that S2 possessed no alkali-silica reactivity. The expansions of the mortars with S6 and S7 were greatly reduced to reach the range below 0.1% without causing any cracks in the surface of the mortars. However, they still caused a higher expansion than S2; the mortar with

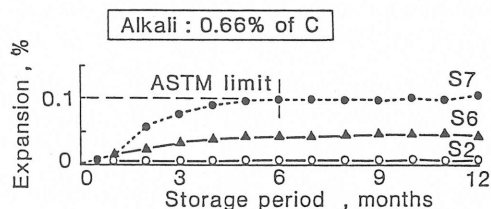


Fig.14 Results of mortar-bar test (no NaOH added).

S7 showed a nearly equal expansion to the ASTM limit. Judging from all of the above results, it is conceivable that S2', S2, S4 and S5 are quite innocuous, while S6 and S7 may cause an undesirable effect due to alkali-silica reaction in concrete depending on their conditions of use. S3 may react with alkalis in concrete, but the resulted expansion will not cause any serious deterioration of concrete. Hasaba et al.[3] reported that the only slag they used in their experiment caused a high expansion of mortar due to alkali-silica reaction such a result might have been obtained probably because the same kind of slag as S6 or S7 was used in their experiment and its reactivity was accelerated by their test conditions.

As shown in Table 2, there is almost no difference in the chemical compositions of the slags except that S4 and S5 contain a little more CaO than the others. Therefore, it is expected that the cooling temperature and/or cooling rate of their original molten slags were somewhat different one another and resulted differences in their mineral compositions caused the remarkable differences in alkali-silica reactivity. In order to examine this possibility, all the slags were ground into powders and analyzed by X-ray diffraction.

According to the results of X-ray diffraction analysis (Fig. 15), the slags can be classified into three groups depending on the peaks of crystalline minerals contained in them; namely, those which contain only forsterite (Group I), those which contain forsterite and enstatite (Group II), and those which contain diopside in addition to forsterite and enstatite (Group III). Table 5 summarizes these groups and names of slags in each group. When Table 5 is compared with the previous results, an interesting tendency can be found. That is, all the innocuous slags belong to either Group II or III, while those slags that caused higher expansions of mortar than the innocuous ones all belong to Group I.

According to MgO-SiO₂ phase diagram [18] shown in Fig. 16, the range of temperature where only forsterite appears in the liquid phase is higher than that where the minerals of Group II (forsterite and enstatite) are formed in the composition range where only these two minerals are formed. This would imply that the slags in Group I were started to be chilled at a higher temperature than those in Group II and contained some glassy phase in addition to forsterite. The slags in Group III are considered to have been chilled nearly

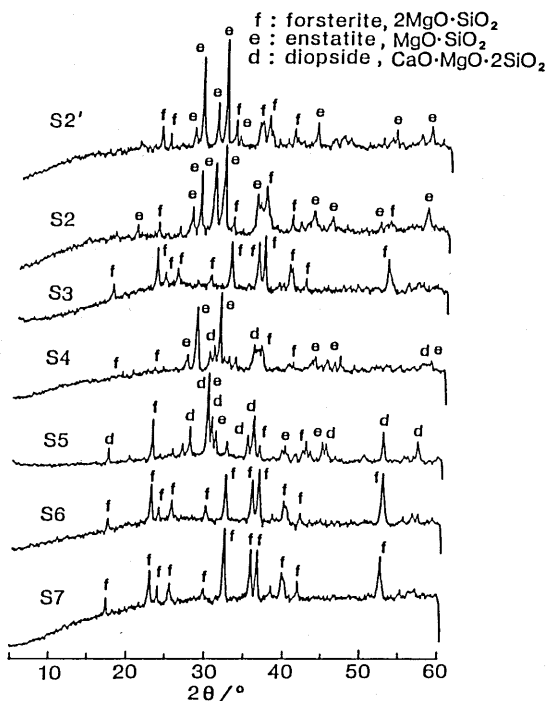


Fig.15 Results of X-ray diffraction (Cu, K α radiation).

Table 5 Classification of slags.

	CLASSIFICATION		
	I	II	III
CRYSTALLINE MINERALS	F	E, F	E, F, D
SLAG	S3, S6, S7	S2, S2'	S4, S5

F:FORSTERITE, E:ENSTATITE, D:DIOPSIDE

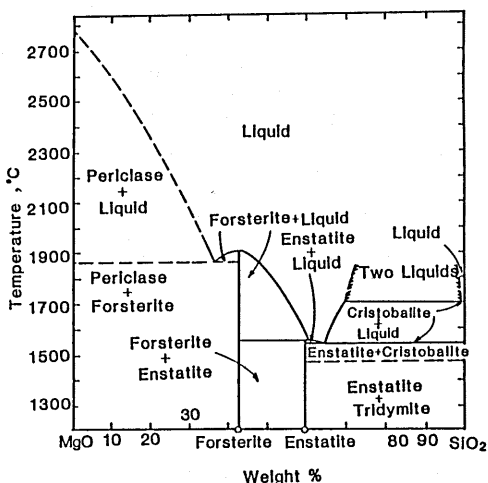


Fig.16 Phase diagram of MgO-SiO₂.

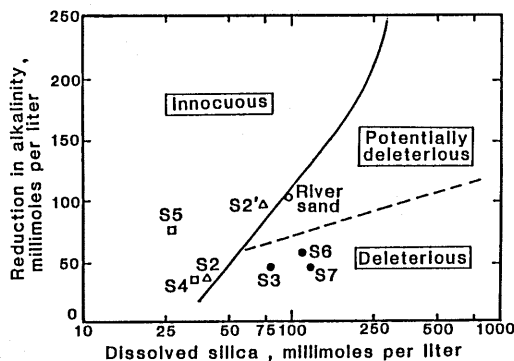


Fig.17 Dissolved silica vs. reduction in alkalinity.

in same way as the slags in Group II because enstatite is the common mineral to these groups, although Group III slags contains diopside in addition to the minerals of Group II due to their relatively high CaO content. Then, the slags in Group III would contain only a little amount of glassy phase if any. Here it should be mentioned that forsterite, enstatite, or diopside itself is unlikely to be reactive because all of these minerals exist in the innocuous slags. Therefore, it is considered that the potential alkali reactivity of the slags in Group I was caused by the existence of glassy phase in them formed by rapidly chilling during their production.

Although the mineral compositions of reactive slags were identified in the above discussion, the reason for the differences in the alkali reactivity of the slags in Group I still remains unexplained. This was investigated by performing a modified test of ASTM C 289 (Chemical Method) for all the slags. The gradings of samples in this test were made exactly the same as those used in mortar specimens in Fig. 13, and the samples immersed in NaOH solution were kept for 4 weeks at 38 C. Fig. 17 shows the test results plotted in the relation between dissolved silica and reduction in alkalinity. The boundary lines specified in ASTM C 289 for judging alkali reactivity of aggregate are also drawn in the figure for reference.

According to Fig. 17, the slags whose data points lie in the deleterious zone of ASTM are only those in Group I, i.e., S3, S6 and S7. It is also observed that the amount of dissolved silica is high in the order of S7, S6 and S3, regardless of the nearly equal reductions in alkalinity of their immersed solutions. These results would suggest that the slags in Group I are reactive in the order of S7, S6 and S3. This order coincides with that of the reactivity observed in the mortar bar test. Therefore, it is conceivable that the observed differences in the alkali-silica reactivity among the slags in Group I are due to the differences in the amount of unstable amorphous silica in them caused by their somewhat different chilling process, although they were rapidly chilled from the temperature range where only forsterite and glassy phase existed. The much lower alkali-reactivity of S3 than that of S6 or S7 would be explained by its

low dissolution of silica in alkali solution; the amount of dissolved silica from S3 being about two-thirds that from S6 or S7.

It may be interesting to note that the data points of S2', S2, S4 and S5 which were confirmed innocuous in the previous mortar test all lie in the innocuous region in Fig. 17, and the result of river sand which caused a little high expansion of mortar lies close to the boundary between the innocuous and potentially deleterious regions, regardless of the fact that these results were obtained through a much moderate test method compared with the ASTM procedures.

(2) Stability of Slag in Concrete

In order both to confirm the above results on alkali-silica reaction for the case of concrete and to examine the possibility of expansion due to free MgO in slag, concrete specimens (100x200mm cylinders) were made and cured under water for 7 days at 20 C, and then placed under three environments; outdoor exposed to natural weather condition, under water controlled at 20 C and 50 C. The water-cement ratio of concretes was fixed at 50%. The slags used in the test were air-granulated slag (S2) and three water-granulated slags (S4, S5, and S7) whose furnace types were different one another. Concrete specimens made with S4 were placed only under water at 20 C.

At present, none of the specimens placed outdoors or under water at 20 C show any unusual features such as cracks or others after about 2 years of storage. However, popouts of slag particles were observed to occur in the surface of specimens with S2 and S7 after about 3 months of storage when the specimens were stored under water at 50 C (See Photo 2). All the popout particles were either white or reddish brown in color, which was quite different from the colors of original slag particles. In order to examine the cause of the popout, the popout particles were removed from the concrete specimens and analyzed by X-ray microanalyzer for their chemical compositions. The removal of particles was made after the concrete specimens were washed by running tap water for about 24 hours. The particles of S7 could be removed in their original form, but those of S2 only in a powder form because they were quite soft.

Table 6 summarizes the results of the analysis made at a center part of the popout particle of S7 and for the powder sample of S2 expressed in oxide forms. As seen in Table 6, the chemical compositions of popout particles are quite different from the average compositions of original slags shown in Table 2. It should be noted that more than 80% of the sample S7 is composed of MgO. The actual MgO content of the sample S2 would be also considerably high, if one considers that original S2 itself contains only a trace of CaO and, therefore, the high CaO content in Table 6 is due to the possible inclusion of cement hydrates in the powder sample. Therefore, it is expected that some particles of original S2 and S7 were composed of free MgO and combined with water to swell

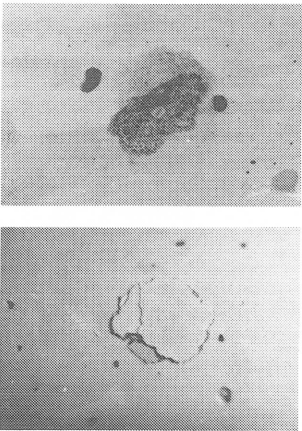


Photo 2 Popout of slag-particle.

Table 6 Chemical compositions of popout particles.

SLAG	CHEMICAL COMPOSITION , %					
	MgO	CaO	FeO	SiO ₂	Al ₂ O ₃	OTHERS
S 2	41.5	44.8	3.3	3.8	3.2	3.4
S 7	82.3	3.0	4.7	6.0	4.0	0

themselves causing their popout. This possibility was investigated by embedding slag particles of various colors in cement paste (15x20x15mm) and immersing the paste sample under 50 C water saturated with Ca(OH)_2 . However, no changes can be seen so far after about 1 year's immersion. Further investigations will be required to clarify the cause of popout.

One would expect that the popout of slag particles may be a result of alkali-silica reaction at least for the case of S7 because it is most reactive with alkalis. However, no such evidence of the reaction as gel exudation or reaction rim was observed around the popout particles at all. It should be also mentioned that S2 was not alkali reactive, although popout was observed when it was used in concrete. In addition, the popout particles contained only several percent of SiO_2 (See Table 6). Considering these facts, it is unlikely that the popout was caused by the alkali-silica reaction of slag particles.

7. CONCLUSIONS

All the slags obtainable in Japan were studied for their feasibility of being used as fine aggregate in concrete. Within the limits of the experiments, the following conclusions can be drawn.

- (1) The optimum sand-aggregate ratio of concrete made with water- or air-granulated slag is 0 to 3% less than that with river sand. The sand-aggregate ratio needs to be lowered as the angularity of slag particles is increased. This is contrary to the general belief that sand-aggregate ratio must be increased when crushed fine aggregate is used. When angular fine aggregate is used, however, it is considered logical to decrease the sand-aggregate ratio as proposed in the present study, or increase the amount of fine materials such as cement and/or mineral admixtures, because the workability of concrete would be improved as the influence of undesirable factors, i.e., angularity of aggregate, is lessened. For air-cooled slag, on the other hand, the optimum sand-aggregate ratio was about 10% less than that for river sand, because it contained an excess amount of powders and fine grains.
- (2) The water requirement of concrete with air- granulated slag can be reduced by more than 10% compared with the case with river sand due to its spherical shape and smooth surface. On the contrary, the use of air-cooled slag or most of water-granulated slags, whose particles are angular, generally increases the water requirement by about 15% at maximum, although the extent of which becomes smaller as water-cement ratio is increased. Some water-granulated slags possess larger solid volume percentages and require less water than river sand regardless of their angular shape.
- (3) In general, the properties of slag concrete in its fresh stage such as air entrapping characteristic, bleeding and setting time are qualitatively similar to those of concrete with granulated blast furnace iron slag. The only difference is that using air-granulated slag also increases the amount of entrapped air in plain concrete. About 1% increase in entrapped air was observed through its use in the present study. Although it was found that the increased air was partly caused by about 10% lower cement requirement of air-granulated slag concrete than river-sand concrete, the main reason could not be clarified. Air-cooled slag which contains a large amount of fines requires two to three times more air-entraining admixture to be added in concrete compared with the case of using river sand.
- (4) The compressive strength of slag concrete within 6 months of age is a little lower than that of ordinary concrete at a fixed water-cement ratio. The rate of

increase in strength of slag concrete at later ages is similar to that of river-sand concrete, because the latent hydraulicity of slags is negligible.

(5) The freeze-thaw resistance of slag concrete is generally lower than that of ordinary concrete at a fixed air content. The increased bleeding of slag concrete is mainly responsible for the low freeze-thaw resistance. When the increase in bleeding water is remarkable, the reduced freeze-thaw resistance can not be improved at all by increasing the air content. Therefore, the bleeding of concrete should be reduced to the lowest possible level by proper means in addition to sufficient air-entrainment, when the slag is used in concrete to which a satisfactory freeze-thaw resistance is required.

(6) At present, about half of the slags obtainable in Japan will not impair long-term stability of concrete when they are used as its fine aggregate. However, the rest slags may cause alkali-silica reaction and/or grain popout in concrete depending on their conditions of use or environment.

(7) Slags which are rapidly chilled from their molten stage and composed of only forsterite and glassy phase may cause a reaction with alkalis in concrete, while those slags which are moderately cooled and contain enstatite and/or diopside in addition to forsterite are stable.

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