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ALKALI-SILICA REACTIVITY OF FERRO-NICKEL SLAGS

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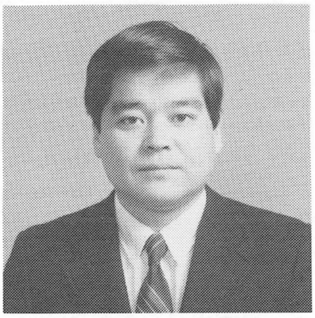

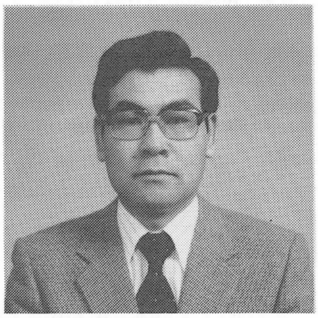

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SYNOPSIS

Experiments were conducted to generally clarify the alkali-silica reactivity of ferro-nickel slags. The slag samples tested include one slag that was found to be most reactive in the previous study, three samples prepared by heating the most reactive slag again up to 700, 1000 or 1100 C, and one glassy slag. The slags which were composed of only forsterite and glassy phase and contained little CaO as their compositions were found to be reactive. In the case of these slags, amorphous silica in them was considered to be responsible for their reactivity. The existence of about 15% CaO in a slag greatly suppressed the dissolution of silica into alkali solution, thereby making the slag innocuous. The reactive slag could be converted to innocuous one by heating it again at 1100 C. Replacing a part of cement with such mineral admixtures as fly ash and blast furnace slag was quite effective in reducing the expansion of concrete due to alkali-silica reaction.

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1. INTRODUCTION

The authors have conducted a series of study on the effective utilization of ferro-nickel slags (hereafter, they will be called simply as slags) as a fine aggregate for concrete, and reported already that about a half of the slags currently discharged in Japan could be used as concrete aggregate provided the mix proportions of concrete were properly selected [1]. The rest of the slags had possibility of causing alkali-silica reaction and/or popout in concrete. It was also shown that the alkali-reactive ones contained a considerable amount of amorphous silica due to their rapid chilling from a quite high temperature.

The present paper discusses the results of further study conducted to generally clarify the alkali-silica reactivity of slags, using heat-treated slags that were obtained by heating the most reactive slag again at 3 different temperature levels and also using a completely glassy slag. Both the means of utilizing the reactive slags and the applicability of ASTM C 289 (Chemical Method) for judging the alkali-silica reactivity of slags were also examined briefly.

2. MATERIALS AND EXPERIMENTAL WORK

Slag samples mainly used in the study include, S7 which were found to be most reactive in the previous study, three slags which were produced by heating S7 again in a muffle furnace, and a completely grassy slag (S5') which were drawn from the same blast furnace as S5 in the previous study. In producing the heat-treated slags, S7 was heated in the furnace for 2 hours at 700, 1000, or 1100 C and, then, cooled gradually in the furnace to room temperature. These heat-treated slags will be called A, B, or C, respectively. In some parts of the study, other slags were used. Their quality and names are exactly the same as those in the previous paper [1]. For the purpose of combined use with the slags and/or comparative purpose, Kinu River sand (specific gravity = 2.59, absorption = 2.27 %), Kasama crushed sand (hard sandstone, specific gravity = 2.61, absorption = 1.25 %) and blast-furnace slag fine aggregate (specific gravity = 2.60, absorption = 1.73 %) were also used.

Three different brands of cement conforming to ASTM Type I were used. Their alkali contents were 0.57, 0.66, and 1.03 % in sodium oxide equivalence (See Table 1). In some parts of the experiment, two kinds of blast-furnace slag powders (B1, B2) and two kinds of fly ashes (F1, F2) were used, the properties of which are shown in Table 2.

The alkali reactivity of slags was tested in accordance with either ASTM C 227 (Mortar-Bar Method) or ASTM C 289 (Chemical Method), except that the alkali content in the mortar-bar tests was intentionally increased to 0.66, 1.03 and 1.66 %. The alkali content of 1.66 % was attained by dissolving reagent grade sodium hydroxide in mixing water for mortar in which cement with 0.66 % alkali content was used. In the chemical method, an ultraviolet spectro-photometer was employed.

Table 1 Properties of cements.

Cement	Chemical composition , %									Specific gravity	Specific surface (cm²/g)	Compressive strength(MPa)		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Na_2O eq.			3d	7d	28d
1	22.1	5.5	3.0	64.9	1.4	1.8	0.28	0.44	0.57	3.16	3240	13.8	22.5	40.3
2	22.2	5.4	3.1	65.1	1.2	1.9	0.33	0.50	0.66	3.16	3210	13.9	22.7	40.3
3	22.3	5.1	3.0	63.2	1.7	1.9	0.54	0.74	1.03	3.15	3430	13.2	22.5	37.0

In the part of experiment where the effect of the addition of mineral admixtures on alkali-silica reaction was studied, concrete specimens (10x10x40 cm) were made to measure their length change. In this experiment, cement with 0.57 % alkali content was used and a proper amount of sodium hydroxide added to obtain concrete of equal alkali content to that in which only cement with 1.3 % alkali was used. The mixing of concrete, preparation of specimens and measurement of length change were all conducted in a temperature controlled room at 20 C. The specimens were demolded at 3 days, measured for their initial lengths and, then, brought in a controlled room at 50 C and 85 % R.H. to accelerate the alkali-silica reaction. These specimens were always in a moist condition because they were wrapped with wet cloth and placed in a sealed box in which only its bottom portion below the specimens was filled with water. The length change measurement was made by a dial gauge type comparator.

3. RESULTS AND DISCUSSION

(1) Characteristics of Mineral Compositions of Reactive Slags

Fig. 1 shows the results of mortar bar tests performed at three different alkali levels (0.66, 1.03 and 1.66 %) using the heat-treated slags at 700, 1000 and 1100 C and their original slag (S7). It is seen in the figure that the expansion of mortar containing the heat-treated slag at 1100 C is less than a half of the limit given in ASTM C 227 (0.1 % at 6 months) at any alkali level, probably indicating that the alkali reactivity of the heat-treated slag at 1100 C was improved remarkably. However, the heat-treatment at 700 or 1000 C did not improve the reactivity at all. That is, the expansions of mortars with these slags were nearly the same as that with original slag (S7), and reached

Table 2 Properties of mineral admixtures.

Type	Name	Specific gravity	Specific surface(cm^2/g)	ig.loss (%)
Blast * furnace slag	B1	2.90	4410	0.2
	B2	2.89	4500	0.1
Fly ash	F1	2.15	3650	0.5
	F2	2.21	5130	3.5

* Ground powder of water granulated iron-blast-furnace slag. B1 and B2 contain 0 and 2% $CaSO_4 \cdot 2H_2O$, respectively.

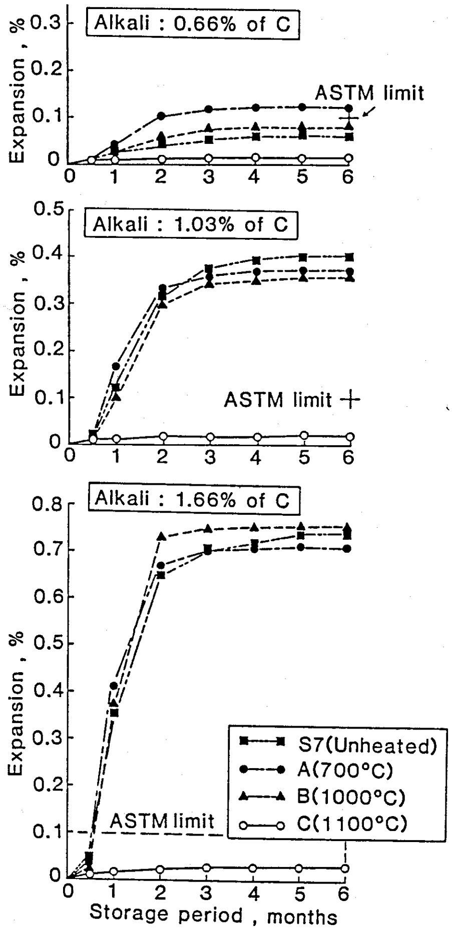

Fig. 1 Results of mortar-bar test.

almost the same level as the ASTM limit (0.1 %) even when the alkali content was relatively low (0.66 %). When alkali content was increased to 1.03 or 1.66 %, their expansions at 6 months were 3.5 to 7 times larger than the ASTM limit.

Uomoto et al. [2] examined the alkali reactivity of the same heat-treated slags as those in the present work in mortar specimens that were cured both under a high temperature condition and by autoclaving, and obtained similar tendency to the above. However no reason was shown why only the slag treated at 1100 C did not possess alkali reactivity. Therefore, mineral compositions of slags were examined next by the powder method of X-ray diffraction to seek for the reason.

Fig. 2 shows the X-ray diffraction patterns of the heat-treated slags and S7, along with the pattern of innocuous S2 (air-granulated slag) whose chemical compositions are nearly the same as those of S7 for a comparative purpose. It is seen that the heat-treated slags contain enstatite in addition to forsterite as in the case of S2, while their original slag S7 contains only forsterite as crystal minerals. It was concluded in the previous paper [1] that those slags containing both forsterite and enstatite were innocuous. This conclusion will appear to be in contradiction to the results of the present work in that the heat-treated slags at 700 and 1000 C were reactive regardless of the existence of both minerals. However, the apparent contradiction may be explained as follows.

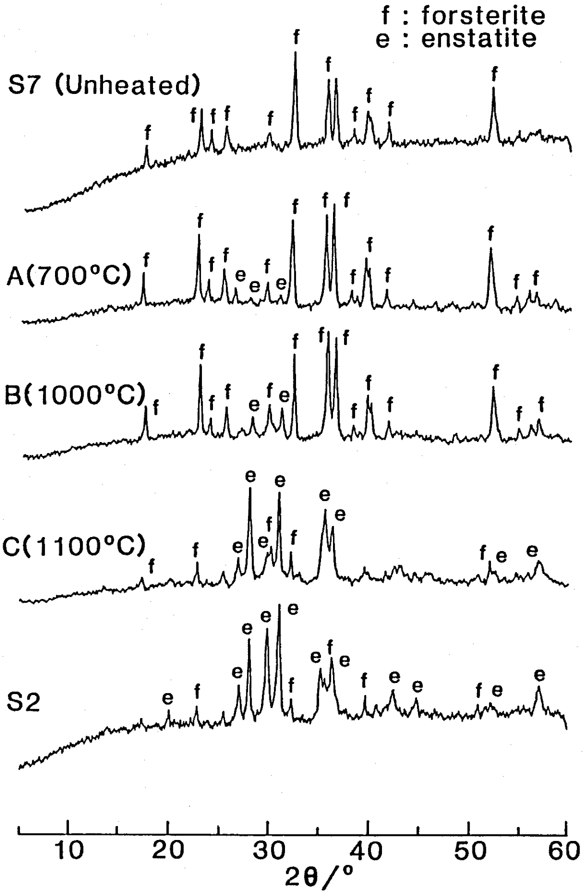

Fig. 2 Results of X-ray diffraction. (Cu, Kα radiation)

Referring to Fig. 2, it is observed that the peaks of enstatite are much weaker than those of forsterite in the cases of the slags which were treated at lower temperatures than 1000 C and caused a large expansion of mortar. On the other hand, when heated to 1100 C, the growth of enstatite peaks is prominent and overall X-ray pattern became quite similar to that of S2 which was confirmed to be innocuous. These results will imply that most of the glassy phases existed in S7 transformed into non-reactive mineral (enstatite) when treated at 1100 C, whereas only a small portion of the grassy phases transformed into enstatite when treated at lower temperature than 1000 C. Judging from these results, therefore, it may be concluded that a considerable amount of grassy phase remains in the reactive heat-treated slags and the remaining grassy phase was responsible for the observed reactivity.

In order to confirm the above discussion, an additional slag sample S5', which was taken from the same furnace (blast-furnace) as S5 and consisted of only glassy phase as shown in Fig. 3, was tested for its reactivity by mortar-bar test at alkali content of 1.66 %. The result is shown in Fig. 4 together with that of mortar containing only river sand as fine aggregate. It can be seen in Fig. 4 that the expansion of mortar containing S5' at 6 months is only one fourth of the ASTM limit and is even smaller than that of mortar with river sand. This result is not in line with the above conclusion. However, the reason why such a contradictory result was obtained may be explained by the peculiarity of the chemical compositions of S5'. As shown in Table 3, S5' which was drawn from blast-furnace contains exceptionally large quantity (about 14 %) of CaO compared with other slags from electric furnaces, because limestone is added as a raw material in the blast-furnace. Here, it should be mentioned that blast-furnace slags in iron production, which contain a great amount of CaO as their chemical component as its example also shown in Table 3, do not cause alkali-silica reaction regardless of their quite amorphous property. Considering these facts, it is expected that CaO in S5' or iron slags may be playing a role of suppressing the reactivity of amorphous silica. To confirm this expectation and aforementioned results of mortar-bar test, the ASTM chemical test was conducted for all the slags including blast-furnace iron slag (BF).

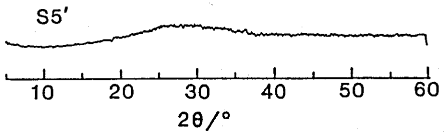

Fig. 3 Result of X-ray diffraction for S5'. (Cu, Kα radiation)

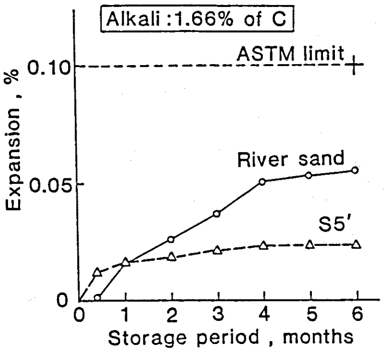

Fig. 4 Results of mortar-bar test.

Fig. 5 shows the results of test by ASTM Chemical Method. It is seen in Fig. 5 that the glassy slag S5' and BF, which contain a large amount of CaO, released only a small amount of silica, and that their data points lie in the innocuous region specified in ASTM C 289. These results will suggest that CaO in glassy S5' and BF suppresses the release of their grassy silica into alkali solution, making them innocuous.

Table 3 Chemical compositions of slags.

Type	Furnace	Chemical composition , %						Slags
		SiO_2	MgO	CaO	FeO	Al_2O_3	Others	
Ferro-nickel slag	Electric furnace	52.5 〜 56.0	33.7 〜 37.0	0.2 〜 1.5	5.4 〜 9.0	1.2 〜 2.9	0.5 〜 1.3	S2,S2' S3,S6,S7
	Rotary kiln	54.1	28.4	5.5	7.7	2.4	1.9	S4
	Blast furnace	50.6	26.0	14.3	4.4	3.7	1.0	S5',S5
Iron slag*	Blast furnace	34.2	6.8	41.3	0.7	13.7	3.3	BF

* Water granulated iron-blast- furnace slag.

In the cases of reactive slags such as S7 and heat-treated slags at a lower temperature than 1000 C, the amount of dissolved silica was more than 3 times that of the heat-treated innocuous slag (C) as can be seen in Fig. 5. It is also seen in the figure that a larger quantity of silica was released into the solution as the treating temperature was raised. These results are considered to give a confirmation to the previous speculation for the slags containing little CaO that a considerable amount of glassy phase remains in the heat-treated reactive slags (A and B) and the glassy phase is responsible for the alkali-silica reaction.

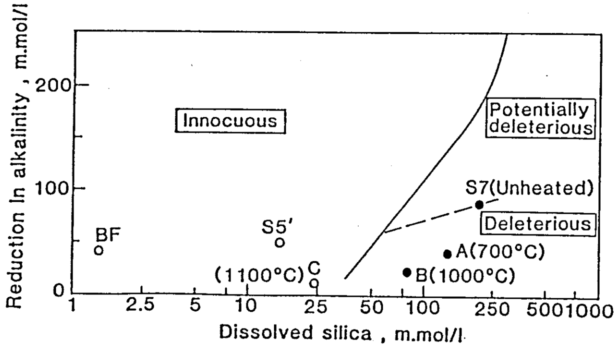

Fig. 5 Dissolved silica vs. reduction in alkalinity.

(2) Effective Means of Utilizing Reactive Slags

It was shown in the previous section that reactive slags could be converted into innocuous ones by either heating them again to crystallize all of the grassy phase or increasing their CaO content. However, these means are not practical, because the former requires a great amount of additional energy and the latter reduces further the current efficiency of ferro-nickel production in which only 2 to 3 % of raw materials are being taken out as ferro-nickel. Another conceivable way of producing stable slag is to lower the temperature of liquid-form slag before its chilling. However, this procedure is too dangerous to be employed in the cases of slags drawn from electric furnaces in which no source of CaO is intentionally added, because of possible explosion due to the increased viscosity of slag. Thus, all the conceivable and effective ways of converting the reactive slags into stable ones are quite difficult to be employed at present. Therefore, other effective means of utilizing reactive slags as concrete aggregate were studied next.

The combined use of reactive slags with stable aggregate will be one of the means of reducing the expansion of concrete. However, it is known that many reactive aggregates often induce the largest expansion in concrete when they are used in combination with stable ones in a certain mix proportion [3]. Such mix proportion at which the largest expansion occurs is frequently called "pessimum content". The existence of such pessimum content were, therefore, examined for the cases of reactive S6 and S7 by combining them with innocuous river sand.

Fig. 6 shows the test results expressed in the relation between slag content in fine aggregate and expansion of mortar at 6 months for the case of alkali content of 1.03 %. It is observed that the expansion increases as the slag content increases, indicating the existence of no pessimum content. This tendency is also seen in the work by Hasaba et al. [4], in which the same kind of slag as those in the present work was tested although the alkali content in their test is not shown.

It is generally believed that the expansion of concrete or mortar due to alkali-silica reaction is brought by gels which are composed of relatively large amount of alkali metals such as Na and K, and that those gels which are rich in Ca but poor in Na or K are stable [5]. When reactive aggregate is used together with non-reactive one in concrete, the following two effects can be expected. Firstly, the alkali concentration per unit volume of reactive aggregate increases and, therefore, the probability for the highly expansive gels to be produced also increases. This will be a positive factor to increase the expansion. The second effect is the reduction in the amount of expansive gels due to reduced volume of reactive aggregate, which is considered to be a factor to decrease the expansion. Then, whether or not pessimum content exists will be a matter of balance between these two effects. In the cases of reactive slags in the present study, it is expected that highly expansive gels are produced under high alkali condition, because the expansion of mortars containing them increased almost linearly as their alkali content was increased as shown in Fig. 7. Regardless of such a highly expansive property of the gels, the curves in Fig. 6 are convex downward and the expansion increased sharply when the slag content was made 100 %. These results would suggest that there will be no pessimum content when S6 or S7 is used together with stable aggregate at least at such alkali levels that are contained in ordinary cement.

Further examination of Fig. 6 reveals that the expansion of mortar with S7 is smaller than the ASTM limit (0.1 %) when the slag content is less than 40 %. In the case of S6, it induced nearly equal expansion to the ASTM limit at 100% slag content; at other slag content, the resulted expansion is less than the limit. These characteristics and the previous result that pessimum content does not exist are beneficial in considering the utilization of reactive slags. That is, if these characteristics are utilized and proper slag content is selected, the reactive slags could be used as concrete aggregate together with stable aggregate without causing serious expansion in concrete. The proper slag content in this case must be determined considering the materials to be used, environmental conditions, and other related factors to alkali-silica reaction. However, it is recommended to use the slags at lower slag content than 30 % for safety in general cases, judging from the results in Fig. 6 that were obtained under relatively higher alkali condition (1.03 %) than ordinary condition.

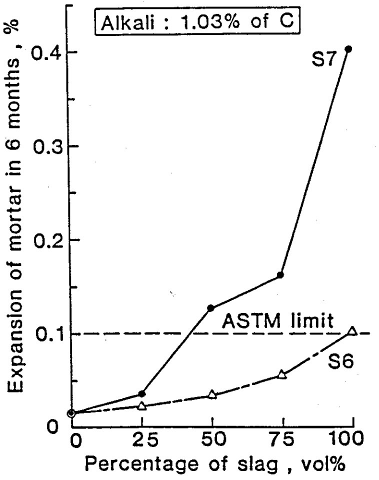

Fig. 6 Slag content vs. expansion of mortar. (6 months)

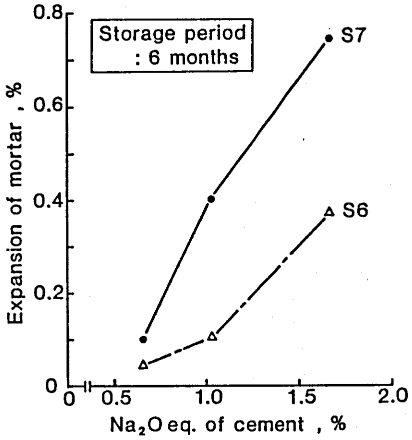

Fig. 7 Alkali content vs. expansion of mortar. (reactive slags)

It is known that alkali-silica reaction of ordinary aggregate can be suppressed by the addition of such mineral admixtures as blast-furnace slag powder and fly ash [3]. Therefore, another series of experiment was conducted to examine the effect of these admixtures on the alkali-silica reaction of reactive slags. The experiment was carried out on concrete specimens and the most reactive slag S7 was used as fine aggregate. For coarse aggregate, crushed limestone (maximum size = 20 mm, specific gravity = 2.72, fineness modulus = 6.77) was used. The unit cement content, water-cement ratio and sand-aggregate ratio of reference concrete, in which no admixture was added, were 320 kg/m^3, 56 % and 46 %, respectively. In the cases of using the admixtures, 30 or 50 % of the cement in the reference concrete was replaced by the equal volume of the admixtures. The alkali content was adjusted so as for the total alkali content in concrete to be 1.3 % of cement by weight.

Fig. 8 shows the results of length change measurement of concrete specimens measured for 9 months under the condition of 50 C and about 100 % R.H. For a comparative purpose, the length change of specimens that were prepared using non-reactive crushed sand (hard sandstone)instead of S7 but with no mineral admixture is also shown in the figure. As can be seen in Fig. 8, the expansion of concrete containing reactive S7 was greatly reduced by replacing a part of its cement with blast-furnace slag powder or fly ash. When the replacing percentage was set at 50 % for blast-furnace slag powder or 30 % for fly ash, the resulted expansion was reduced to the same level as that of concrete with non-reactive aggregate even at 9 months of storage, and no cracks were observed on the surface of these specimens. These results would imply that the reactive slags can be effectively used as concrete aggregate provided that a proper amount of cement in concrete is replaced with these admixtures. The required minimum rate of cement replacement by these admixtures in this case is considered to be about 30 % for fly ash and 50 % for blast-furnace slag powder, judging from the experimental condition that the alkali level selected was 1.3 %, which is a little higher than the maximum alkali content (about 1.1 % [6]) of the cements so far produced in Japan.

It may be added that the fly ash F2 in the figure is rather poor in its quality as an admixture for concrete for general use; it contains many slaggy particles and its loss on ignition is relatively high (See Table 2). Regardless of such poor quality, it reduced the expansion of concrete to the same extent as the quality fly ash F1 did as seen in Fig. 8. This property will be worth noting when the utilization of low quality fly ash is considered.

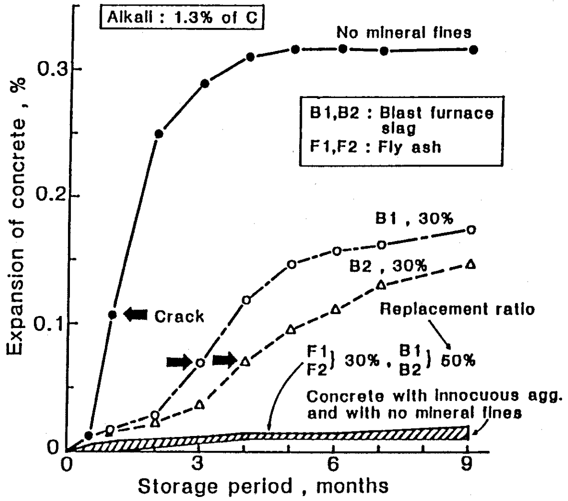

Fig. 8 Effects of mineral admixtures on expansion of concrete containing reactive S7.

(3) Applicability of Chemical Method in Judging Alkali-Silica Reactivity of Ferro-Nickel Slags

In paragraph 17 of ASTM C 289, it is stated that results of the chemical method may not be correct for aggregate containing silicates of magnesium such as antigorite [$Mg_3Si_2O_5(OH)_4$]. However it was shown in 3.(1) that, in the case of S7 and the heat-treated samples of S7 which are composed of silicates of magnesium such as forsterite and enstatite, their reactivity judged by mortar-bar test was in quite good agreement with the results by chemical method. The good agreement between the results by these tests was also observed in the previous study [1] in which the analysis for chemical test was made after immersing samples in alkali solution of 38 C for about 1 months. To confirm these results, all of the slags available in Japan were tested by ASTM C 289 and the results compared with those by a modified ASTM mortar-bar method in which the alkali content was increased to 1.66 % of cement.

The results of the chemical test are plotted in Fig. 9. In this figure, data points for slags that were judged deleterious in mortar-bar test, i.e., those caused larger expansion than 0.1 % at 6 months, are indicated by solid circles, and those judged innocuous by hollow circles. It is seen in the figure that the judgments by both methods agree each other quite well, except the data points for S2' and S4 which lie almost on the boundary lines between innocuous region and potentially deleterious or deleterious region. The non-agreement of the results of S2' and S4 may be due to small errors involved in chemical analysis or a little impropriety in drawing the boundary lines. Another noteworthy point is that all the slags expressed by solid circles in Fig. 9 (S6, S7, A and B) caused a larger expansion of mortar than the ASTM limit (0.1 %) even when they were tested using only cement of high alkali content (1.03 %) without intentionally adding any sodium hydroxide in previous experiment (See Figs. 1 and 6). Judging from these results, ASTM C 289 (Chemical Method) is considered to be employed as effective means for judging the alkali-silica reactivity of ferro-nickel slags, although their mineral compositions are mostly silicates of magnesium.

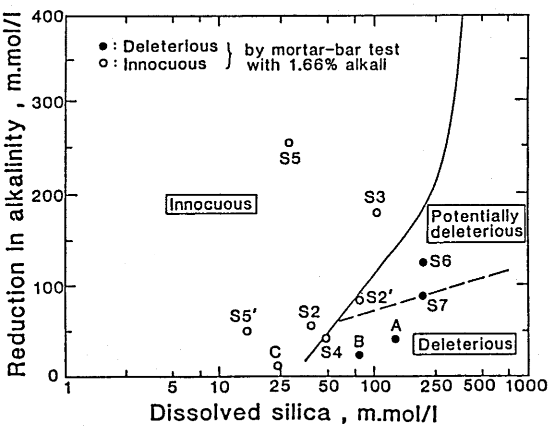

Fig. 9 Results of chemical test. (ASTM C 289)

4. CONCLUSIONS

In order to generally clarify the alkali-silica reactivity of ferro-nickel slags, experiments were carried out using the most reactive slag, heat-treated slags and a completely grassy slag as main samples. Within the limit of the experiments, the following conclusions were drawn.

(1) Alkali reactive slags are those which are composed of only forsterite and grassy phase and contain little CaO as their chemical components. The existence of the glassy phase is responsible for the reactivity. The amount of dissolved silica from these reactive slags into alkali solution is considerably large.

(2) A kind of slag which contains about 15 % CaO does not possess alkali-silica reactivity even if it is completely amorphous. In the case of this kind of slag, the dissolution of silica into alkali solution is quite low, possibly because CaO is playing a role of suppressing the release of silica into the solution as in the case of blast-furnace iron slag.

(3) Alkali reactive slags can be converted into innocuous ones by heating them again to 1100 C and holding them at the temperature for a proper length of time and, then, cooling gradually. This is because almost all of the grassy phases in them transform into crystalline minerals. At lower temperatures than 1000 C, the crystallization of glassy phase is too slow to improve the reactivity.

(4) Under such alkali conditions as those brought in concrete by the use of ordinary cement on the market, the expansion of mortar increases as the proportion of reactive slag in the combined aggregate with non-reactive one is increased, and there exists no pessimum content at which the maximum expansion occurs. When slag content in the combined aggregate is less than 30 %, the resulted expansion is less than a half of the ASTM limit even if the most reactive slag is used. Taking these into account, it is possible to utilize the reactive slags as concrete aggregate by combining them with non-reactive ones in a proper ratio without causing undesirable effects.

(5) The alkali reactivity of slags can be suppressed by replacing a part of cement in concrete with blast-furnace slag powder or fly ash, just in the same way as natural reactive aggregates. The required rate of replacement for completely suppressing the expansion due to the reaction was 50 % for blast-furnace slag powder and 30 % for fly ash in the present study.

(6) It is stated in ASTM C 289 (Chemical Method) that the result by this method may not be correct for aggregate containing silicates of magnesium. However, it is quite effective means for judging the alkali-silica reactivity of the slags under the present study, although they are mainly composed of silicates of magnesium such as forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$) and their glasses.

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