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論　文

［1147］　生コンクリート中のスラグ置換率の定量方法について

APPLICATION OF SELECTIVE DISSOLUTION METHOD FOR THE DETERMINATION OF SLAG ADMIXTURE REPLACEMENT RATIO IN FRESHLY-MIXED CONCRETE

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1. INTRODUCTION

In recent years, the ability of concrete to withstand alkali-aggregate reaction, salts or sea-water attacks has been called for, and the use of ground granulated blast-furnace slag, which is mixed within the concrete mixer as a cementitious admixture, has attracted attention. It is important, however, in terms of execution and quality control of the work to ascertain that slag is used accurately in a prescribed amount. This study relates to test methods for determining the slag replacement ratio in cementitious materials by which samples of concrete are taken in the stage of fresh concrete.

2. OUTLINE OF TESTS

For the determination of the slag content of fresh concrete, there are available selective dissolution methods(1), and the authers judged the salicylic acid-acetone dissolution method(2) to be convenient and provide high accuracy, and first applied to unhydrated cementitious materials. In the next step, to develop a test method for determining the slag replacement ratio in cementitious materials in fresh concrete on job sites by the selective dissolution method, a quantitative analysis of the slag replacement ratio in paste and in mortar was conducted, and also an examination was made as to the effect of the progress of the hydration for two hours after mixing on analytical values of slag replacement ratio. After these preliminary tests, a test was conducted on concrete in a laboratory in the third step and it was ascertained that this method can be applied also to concrete. Finally, paste was extracted in accordance with JIS A 1112 "Method of Test for Washing Analysis of Fresh Concrete" from concrete shipped to a construction site from a ready-mixed concrete plant. Water was removed in situ from this paste with acetone cleaning to stop hydration and with the succeeding drying in an oven

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to ensure the perfect dehydration. And dried samples were shipped to a laboratory to determine the slag replacement ratio by the salicylic acid-acetone dissolution method.

3. APPLICATION OF SELECTIVE DISSOLUTION METHOD

3.1 PRINCIPLE OF SALICYLIC ACID-ACETONE DISSOLUTION METHOD

The salicylic acid-acetone dissolution method is based on the fact that almost all of hydrates and a limited amount of unhydrated portland cement dissolve in salicylic acid, while the glassy unhydrated slag does not dissolve in it.

The unhydrated slag content of cementitious materials of fresh concrete is derived from the following equation when a mixed sample of slag and portland cement (about 0.5g) is dissolved in mixed solution of salicylic acid, acetone and methanol (2.5g of salicylic acid, 35mℓ of acetone and 15mℓ of methanol).

$$\mathrm{Wo} = \mathrm{GS} + \mathrm{PC}, \qquad \mathrm{GS} = \mathrm{Winsol} - 0.211^{*} \cdot \mathrm{PC} \tag{1}$$

* 0.211 is called as Kondo's constant, which is based mainly on the contents of C_3A, C_4AF and $CaSO_4 \cdot 2H_2O$, and this value does not show great variation through the time of hydration and with different types of portland cement.

where Wo : amount of a sample, GS : unhydrated slag content,
PC : portland cement content, Winsol : insoluble residue content (s.a.insol.)

Therefore, slag replacement ratio (SR) is given by the following equation:

$$\mathrm{SR} = \frac{\mathrm{GS}}{\mathrm{Wo}} \times 100 = \frac{1}{0.789} \left\{ \frac{\mathrm{Winsol}}{\mathrm{Wo}} - 0.211 \right\} \times 100 \ (\%) \tag{2}$$

3.2 PROCEDURE FOR SALICYLIC ACID-ACETONE DISSOLUTION

For the salicylic acid-acetone dissolution, the following procedure was applied :

① After putting a sample into an agate mortar and lightly mixing it with a pestle, weigh out about 500mg of the sample accurately to the nearest 0.1mg and put it into an Erlenmeyer flask with a ground stopper (100mℓ).

② Add a mixed solution of salicylic acid, acetone, and methanol to the sample in the flask.

③ With a magnetic stirrer, stir the mixed solution for one hour, making certain that it does not splash. After that, allow the solution to stand for 24 ± 4 hours.

④ Cause the solution obtained in ③ above to be sucked under reduced pressure with a membrane filter placed on the glass-fiber filter paper, and separate the residue on the membrane filter. Then, thoroughly clean the residue with methanol.

⑤ Transfer the membrane filter and the residue to a platinum crucible, heat carefully until the carbon is gone, and then cover and ignite at 850 ± 50℃ for about ten minutes until the weight becomes constant.

⑥ Cool in a desiccator and weigh the crucible with the residue.

3.3 TEST RESULTS FOR UNHYDRATED CEMENTITIOUS MATERIALS

Slag not containing gypsum was used as the sample for the tests and rapid hardening portland cement(RHC) not containing such secondary cementitious constituents as slag was used. Their test values were as follows :

Slag : Specific gravity 2.91, Blaine specific surface area 3890cm^2/g,
Glass content 99%
RHC : Specific gravity 3.13, Blaine specific surface area 4090cm^2/g,
Initial set 2h and 10min, Final set 3h and 35min

The weight of each sample was 500mg. Cementitious materials were prepared by blending in advance at slag replacement ratios of 0, 20, 50, 60 and 100% and the quantitative analysis was made. Results of the analysis are calculated by the eq.(2) and are shown in Fig.1 (see the plots of unhydrated sample). Although slag replacement ratios of 0 and 100% showed some differences between proportioned values and those obtained in the test, good agreement was observed in the case of the other replacement ratios.

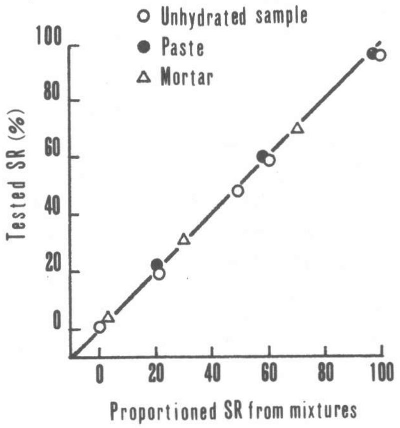

Fig.1 Test Results for Unhydrated Samples, Paste and Mortar

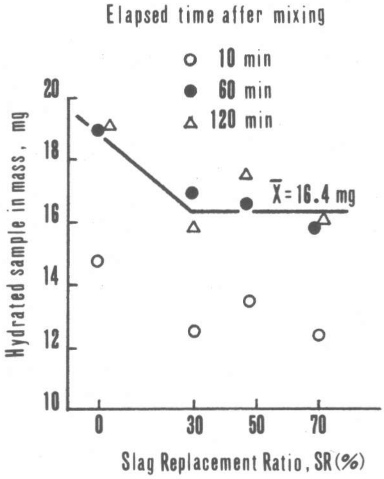

Fig.2 Relation between SR and Hydration with time

4. TEST RESULTS FOR PASTE AND MORTAR

4.1 TREATMENT FOR STOPPING HYDRATION AND OVEN DRYING

The treatment for stopping hydration and oven drying was conducted by the following procedure :

① Mix a sample with water in a glass bottle (30mm in diameter × 40mm, with a cover). After the hydration for a constant time, stop the hydration by adding 15mℓ of mixture of ethyl ether and acetone (1 : 1). (When the hydration time was extended, the paste was remixed at intervals of 20 to 30min in course of hydration.)
② Place the glass bottle in a suction desiccater and cause ether to disperse. After that, transfer it to a draft and cause acetone to disperse completely.
③ After drying the sample at 110℃ in an oven for 3h, cool in a desiccator and weigh the glass bottle with the sample.

4.2 INFLUENCE OF THE TIME OF TREATMENT ON THE PROGRESS OF HYDRATION WITH TIME

The effect of the progress of hydration on the test result was investigated using paste(water-cementitious materials ratio : 0.70) when the time elapsed till the stopping of hydration was 10, 60, 120min. This effect of the time is shown in Fig.2. It should be realized that the degree of hydration is almost constant with no great differences at slag replacement ratio of 30 to 70%, except that the elapsed time after mixing is 10min. Hydration should be stopped as quickly as possible while the degree of slag hydration is still low. However, because it is difficult to stop hydration within approximately 10min after mixing in actual practice, and in view of the transportation of concrete and the time elapsed till the stopping of hydration on job sites, a quantitative analysis can be made in this time zone in which the influence of the time of stopping hydration is small and the degree of hydration is nearly constant. It is appropriate to use the mean value of the test results as the constant correction factor**for the mass of a sample in Eq. (2) by considering this mean value to represent an increase in mass due to combined water by hydration.

** Correction factor $k = 500\,\mathrm{mg} / (500\,\mathrm{mg} + 16.4\,\mathrm{mg})$

$$= 0.968 \qquad (3)$$

4.3 TEST BY PASTE AND MORTAR

The same cementitious materials as used in the test described in 3.3 were used and purified water was used as the mixing water. And in the test of mortar, Toyoura standard sand was used, keeping sand-cementitious materials ratio at 2. For the tests of paste and mortar, the water-cementitious materials ratio was set at 0.70, varying the slag replacement ratios between 0 and 100%.

As shown in Fig.1 (see the plots of paste and mortar), almost the same results as those of the test on unhydrated cementitious materials were obtained.

5. QUANTITATIVE ANALYSIS OF SLAG REPLACEMENT RATIO ON CONCRETE

5.1 TEST FOR STOPPING HYDRATION OF CONCRETE

Since the principle of the determination method is based on the undissolution of unhydrated slag, it is necessary to positively carry out the stopping of hydration. Although the procedure described in 4.1 may be followed in the laboratory, it is difficult in the field to use ether from the stand-point of safety and to conduct filtration in a short time. Therefore, it was decided to reduce the washed suspension solution, from which the supernatant water has been sucked through a siphon, so as to thoroughly clean the samples with acetone and to accelerate filtration by the suction through a simple aspirator using tap water. The effect of the number of cleaning operations with acetone on the interruption of hydration was investigated using ready-mixed concrete. The concrete showed a slump of 12cm, an air content of 4%, and a water-cementitious materials ratio of 0.63. Cementitious materials were prepared by adding extra 15% slag to portland blast-furnace cement Class B(slag content : 40%) and the slag replacement ratio was set at 49%. Slag replacement ratios obtained in the test were 48.35, 48.51, 48.77, and 48.85% when cleaning was conducted twice, three times, four times, and five times, respectively. Thus, the slag replacement ratio tends to increase when the stopping of hydration is positively conducted. But, from a practical point of view in situ, it seems that cleaning three times is sufficient.

5.2 Test Analysis on Concrete and Effect of Fine-Grains of Aggregates

This test was first conducted on concrete mixed by a 40ℓ tilting mixer (called the test batch) at slag replacement ratio of 0, 30, 40(using BFC), 55 and 70%. Then on concrete mixed by a fully automatic batcher plant composed of two 1.5m^3 tilting mixers(called ready mixed concrete) at slag replacement ratio(SR) of 0, 40(using BFC), and 55%. Because the paste portion of the concrete was contaminated with fine-grain portions of aggregates, the amount of materials finer than 0.074mm of aggregates were determined beforehand.

Slag GGS : Specific gravity 2.89, Blaine specific surface area 3600cm^2/g, $SO_3$2.06%
OPC : Specific gravity 3.15, Blaine specific surface area 3260cm^2/g, Initial set 2h and 25min, Final set 3h and 47min
Sea-dredged sand
  for test batch : Fineness Modulus 2.56, Amount of grains finer than 0.074mm 0.65%
  for ready-mixed concrete : Fineness Modulus 2.60, Amount of grains finer than 0.074mm 0.65%
Stone 2005
  for test batch : Fineness Modulus 6.73, Amount of grains finer than 0.074mm 0.36%
  for ready-mixed concrete : Fineness Modulus 6.65, Amount of grains finer than 0.074mm 0.44%

The slump was 8±1cm, the air content was 4±1%, and the cementitious materials content of concrete was 270kg/m^3.

Unit content of each concrete ingredient determined in accordance with JIS A 1112 "Method of Test for Washing Analysis of Fresh Concrete" is shown in Table 1. Test results for concrete and the effect of fine materials of

Table 1. Test Results for Washing Analysis of Fresh Concrete

	Mix Proportions								Results of Wash Analysis			
	SR	W/C	s/a	Unit Content, kg/m^3								
	%		%	W	OPC	GGS	S	G	W	OPC+GGS	S	G
Test Batch	0	0.68	43.7	183	270	0	770	1015	200	246	769	1014
	30	0.67	43.8	180	189	81	773	1015	181	274	778	1017
	40(BFC)	0.66	43.9	178	270		775	1015	165	274	798	1008
	55	0.66	43.9	177	122	148	775	1015	177	257	749	1054
	70	0.65	43.9	175	81	189	778	1015	174	281	770	1012
Ready Mixed Concrete	0	0.68	43.7	183	270	0	770	1015	172	282	794	1012
	40(BFC)	0.66	43.9	178	270		775	1015	175	274	785	999
	55	0.66	43.9	177	122	148	775	1015	169	278	786	1034

aggregates are shown in Fig.3. Slag replacement ratios adjusted with specified mix proportions and with washing analysis results were about 1% lower than those determined from direct calculation without consideration of the effect of fine-grains of aggregates. Incidently, few differences were observed between the values obtained by the mix proportions and those by the washing analysis.

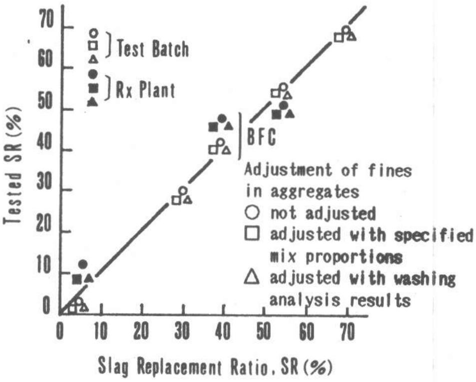

Fig. 3 Test Results for Concrete and the Effect of Fine Materials of Aggregates

6. CONCLUSIONS

A satisfactory determination method of slag replacement ratio in fresh concrete can be established using the washing analysis of fresh concrete and salicylic acid-acetone dissolution method. Because the analysis involves dissolving a sample in a mixed solution of salicylic acid, acetone and methanol, and determining the unhydrated slag content from the amount of insoluble residue, it is important to prevent the sample from reacting before the sample is analyzed after the treatment for stopping hydration. It was ascertained that this problem can be solved by conducting cleaning the sample with acetone three times or more and by employing a suction filtration using an aspirator. If the hydration of a sample stops, it is possible to conduct the salicylic acid-acetone dissolution test on the sample in the laboratory and the slag replacement ratio in fresh concrete can be appropriately determined with some correction of fine-grains contaminated in the paste portion from aggregates used.

Acknowledgements

The tests reported here form part of a larger investigation based on a standardization project of ground granulated blast-furnace slag in the JSCE committee. The authors wish to express their thanks to Professor Shigeyosi Nagataki, the committee chairman, for his kind support.

This paper extends and partially corrects the study outlined and presented elsewhere(3).

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