CONCRETE LIBRARY OF JSCE NO.16, DECEMBER 1990 STUDY ON PROPERTIES OF LOW-HEAT SUPER-FLOWABLE ANTIWASHOUT UNDERWATER CONCRETE









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SYNOPSIS

This paper clarifies the effects of binders and antiwashout admixture on properties such as flowability, setting time, strength, and adiabatic temperature rise of low-heat super-flowable antiwashout underwater concrete based on three-component cement with a large proportion of granulated blast-furnace slag and fly ash. The premise is that the concrete is applied to large-scale underwater structures. Also from a consideration of adsorption of antiwashout admixture by the component materials of the concrete, the effects of adsorption of the antiwashout admixture on the flowability of fresh concrete have been understood and made it possible to obtain an antiwashout underwater concrete with excellent flowability and stable qualities by improving the mixing method. The paper also alludes to peculiarity of the strength and heat generation characteristics of concrete containing the antiwashout admixture.

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1. INTRODUCTION

The utility of antiwashout underwater concrete has been recognized through much research and development as well as actual applications since it was introduced into Japan, and its reliability, resulting from its excellent antiwashout property and self-leveling characteristics when used underwater, has also been confirmed.[1]

Along with the advantage of being able to place good quality concrete directly under water using a concrete pump and placing pipe without the use of any special devices, it has been found useful in important underwater structures such as bridge substructures.

In line with the increase in large-scale structures in recent years, the construction of unprecedented large-scale underwater structures has progressed.[2]

Where a large underwater structure is constructed using antiwashout underwater concrete, the work differs greatly from normal construction, particularly in the following points:

- (1) Long-distance flowability is required since the concrete must be placed through a limited number of placing pipes over a wide area.
- (2) Because it is a mass concrete, the thermal stress due to heat of hydration can present problems.

The necessary long-distance flowability characteristics include the preservation of flowability for many hours, little segregation of materials, and small quality fluctuations due to flow and this makes necessary examinations of materials, mix proportions, and placing.

The thermal stress due to heat of hydration increases with unit cement quantity in antiwashout underwater concrete compared with ordinary concrete, and so it is impossible to carry out curing control as in the case of land-based structures, and it is virtually impossible to repair cracking once it has occurred. Thus it becomes important to control the concrete's exothermic characteristics.

Because the properties of the antiwashout underwater concrete for use in large-scale underwater structures form the primary determinant of the construction plan and the construction equipment needed, it is important to thoroughly understand its basic characteristics.

This study was carried out with low-heat super-flowable antiwashout underwater concrete on the premise that it is applied to large-scale underwater structures. The aim was to clarify its basic characteristics as well as to consider the mechanism by which the antiwashout concrete admixture operates, since this had not been previously made completely clear.

2. SUMMARY OF STUDY

2.1 Necessary Features of Low-heat Super-flowable Antiwashout Underwater Concrete

On the basis of quality of antiwashout underwater concrete required for the Akashi Kaikyo Bridge, the most stringent construction conditions yet called for, the performance of antiwashout underwater concrete was established for the purpose of this study as follows:

- (1) High flowability slump-flow: 52.5 ± 2.5 cm
 - slump-flow retention time: longer than 8 hrs
- (2) Low exothermicity-adiabatic temperature rise: lower than 30°C
- (3) Setting characteristics-initial setting time: within about 30 hrs

2.2 Low-heat Cement for Low-heat, Super-Flowable Antiwashout Underwater Concrete

The low-heat cement chosen is a three-component cement: granulated blast-furnace slag and fly ash blended into portland cement. Ordinary portland cement or moderate heat portland cement was used (referred to as OP for ordinary cement and MP for moderate heat, BS for granulated blast-furnace slag and FA for fly ash). The blending proportion, by weight, of OP, or MP:BS:FA of this three-component cement was in the range 20-35%: 35-45%: 25-40%.

The use of three-component low-heat cements has a considerable history in the construction of important structures, such as underground LNG storage tanks in Japan, and excellent cracking control has always been demonstrated.[3] With regard to durability, it has been confirmed that the cement has excellent properties for salt permeability and drying shrinkage.[4],[5]

2.3 Summary of Experiments

This study consisted of four parts, as described below.

- I: Effect of binders and admixtures on the basic properties of antiwashout underwater concrete.
- II: Effect of the adsorption of antiwashout admixture on properties of antiwashout underwater concrete.
- III: Effect of the mixing method on properties of antiwashout underwater concrete.
- IV: Action of antiwashout admixture in the hardened concrete.

Part I involved examination of the effects of the blending proportion and characteristics of the binders on the basic properties of the antiwashout underwater concrete, such as flowability, setting time, strength, and adiabatic temperature rise. Also the effects of the quantity of AE water reducing agent and superplasticizer used on concrete properties was examined, including the temperature dependence.

Part II involved examining the difference in adsorption characteristics of antiwashout admixture for various combinations of binders and different fine aggregates. From this study, the action of antiwashout admixture in concrete was inferred. The results were used for an examination of the effect of fine aggregate properties on the qualities of antiwashout underwater concrete.

Part III was based on the results of II and involved considering the dispersion mechanism of antiwashout admixture into fresh concrete along with the effect of mixing method on the concrete properties. A new mixing method that yields a concrete of stable quality with excellent flowability was proposed.

In part IV, the effects of antiwashout admixture on the strength and exothermic characteristics of the concrete was examined for various types of cement.

Table 1 shows the types of experiments conducted and the test conditions. The details of the main experimental factors are discussed in later chapters. Tables 2, 3 and 4 show the types and quality of materials used. The symbols given in these tables for the materials are used throughout.

Table 1 Experimental factors and experimental conditions

		,	,	,					Ĺ						
Ехр.		Type of	Blending propor-	W/C	1 1		Unit quantity (kg/m³)		(Cx%)		Surface moist-	Method of mixing			Mixer*1
No.	Experiment	binder	tion PC:BS:FA	*	8	С	W	USCA	S.P.	AEad	ure of aggre- gate	USCA	Dry mixing	Formal mixing	IIIXEI
1- 1	Blending propor- tion of binders	MP1:BS1:FA1		66	40	320	210	2.3	1.0	0.25	S1 0%	Mixed with sand	60S	120S	Pan 1
1-2	Blending propor-	MP1:BS2:FA1		64	40	320	205	2.3	1.0	0.25	S1 0%	"	60S	1205	Pan 1
	tion of binders, BS fineness kinds of MP	MP2:BS2:FA1	25:44:31	66	40	320	210	2.3	1.0	0.25	S1 0%	"	60S	120S	Pan 1
2- 1	Quantity of S.P., AEad	MP1:BS1:FA1	27:40:33	66	40	320	210	2.3		_	S1 0%		60S	120S	Pan 1
2- 2	Temperature, quantity	MP1:BS1:FA1	27:40:33	66	40	320	210	2.3	—	_	S1 0%		60S	120S	Pan 1
3	Measurement of adsorption of anti- washout admixture	OPO, BSa, BSb, FAA, FAB													
4-1	Surface moisture of fine aggregate	MP1:BS1:FA1	27:40:33	66	40	320	210	2.3	1.0	0.25	s1 —	Mixed with sand	60S	120S	Pan 1
	G	MP1:BS3:FA1	30:40:30	68	40	320	219	2.3	1.0	0.25	S2	"	30S	90S	Dual-axis
1 1	Grading of fine aggregate	MP1:BS3:FA1	30:40:30	68	40	320	219	2.3	1.0	0.25	5%	"	-30S	90S	Dual-axis
5-1	Method of adding antiwashout admix-												* 3		
	ture, whether or not dry mixing is done, mixing time	MP1:BS3:FA1	30:40:30	68	40	320	219	2.3	1.0	0.25	S2 5%		(15S)	25-90S	Dual-axis
5- 2	Method of mixing.	OP1:BS3:FA1	20:50:30	67	40	320	215	2.3	1.0	0.25	S3 5%	_	(15S)		Dual-axis
5- 3	Method of mixing and mixing time/	OP1:BS3:FA1	20:50:30	67	40	320	215	2.3	1.0	0.25	S3 5%		(158)		Dual-axis
5-4	Quantity of prima- ry water added.	OP1:BS3:FA1	20:50:30	67	_	509	342	3.66	1.0	0.25	S3 5%	Premix		1805	Epicyclic
6- 1	Type of binders whether or not	OP1, BSa, BS	b, FAA	45	48	400	180	(2.3)*4	1.0	0.10*2	S2 0%	Mixed with sand	30S	1205	Pan 2
6- 2	USCA is present	Combination CaSO, 2H, O, C		45	_	602	271	(2.3)	1.0	0.10	S2 0%	with Sand	60S	180S	Pan 2
6- 3	Pore solution express analysis.	USCA present		45	1:1.5	1:1.5 Cx0.72%		.72%			Stand- ard		60S	180S	Epicyclic
		USCA not pre	sent	45	1:2.0)	Cx0	.72%		_	sand "		60S	1805	Epicyclic

Concrete: Gmax 20 mm, Air volume 4 + 1% (finish of mixing)

*4 Whether or not antiwashout admixture was used.

Table 2 Characteristics of binding materials

Type of	Symbol	Specific gravity	Blaine's specific surface (cm²/g)		ture	Insolu- ble t residue (%)	onemical composition (v)							Heat of hydration		Mineral composi-	
binders							S10,	A1 ₂ 0 ₃	Fe ₂ 0 ₃	Ca0	MgO	SO3	7 days			tion (%) 3S C3A	
Moderate-heat	MP1	3.20	3070	0.8		0.1	24.1	3.6	4.0	63.7	0.7	2.0	260	318	40	3	
portlant cement	MP2	3.20	3120	0.5		0.1	22.9	3.6	4.1	62.9	2.9	1.7	280	327	48	3	
Ordinary portland	ОРО	3.16	3040	0.8		0.2	21.7	5.5	2.8	63.5	1.8	2.0	_		_		
cement	OP1	3.15	3100	0.7		0.3	21.7	5.4	2.7	63.5	1.9	2.0	—	_	_	_	
Granulated	BS1	2.90	3810	1.4	0.1	1.1	32.1	12.8	0.5	41.9	6.2	0.0	Basi	city :	1.90		
slag*1	BS2	2.91	4060*2	1.5	0.1		32.5	13.6	0.7	40.8	8.4	0.0			1.93		
	BS3	2.90	4380	1.3	0.1	_	32.5	13.3	0.4	42.1	7.0	0.0	l		1.92		
	BS-a-3	2.92	4260			_	32.6	14.5	0.4	41.3	6.5	0.2	ŀ		1.91		
	BS-b-3	2.89	4700				30.7	14.6	0.4	41.4	5.6	2.4		:	2.00		
	BS-b-6	2.89	4430				31.5	13.5	0.4	42.6	6.1	1.9			1.97		
Fly ash	FA-1	2.11	3360	1.1	0.1		60.8	27.0	4.0	2.3	1.8		Meth	ylele	blue		
	FA-A-3	2.25	3110	1.4	0.2		51.0	25.1	5.5	9.5	2.5	0.3	1	rption		7	
	FA-B-3	2.13	2450	3.9	0.4	_	55.1	25.9	3.6	5.5	1.5	0.6		(mg/l)	0.2	8	
	FA-A-6	2.25	2970	1.5	0.1	[54.3	_						2		_	

 $^{^{*1}}$ -3: Materials used in experiment 3, -6: materials used in experiment 6, BS-a-6 used was the same as BS3. *2 The different gradings of BS (3200-4100 cm²/g) was adjusted the fineness of the one material

^{**1} Pan 1: Pan type, forced mixing 1001(402/batch), Company T
Pan 2: Pan type, forced mixing 501(201/batch), Company T
Dual-axis: Dual-axis type forced mixing 1001(701/batch),
Company K
Epicyclic: 101 mortar mixer (61/batch)

 ^{*2} AE adjustment agent used so that air volume at the finish of mixing will be 4:1%.
 *3 Whether or not dry mixing was implemented.

Table 3 Characteristics of aggregates

Material	Symbol	Specific gravity	Water absorption (%)	Unit weight (kg/l)	Absolute volume (%)	F.M.
Sea sand (from Ose sea area)	S1 S2 S3	2.54 2.53 2.54	2.20 2.53 2.19	2.53 1.57 1.53	63.1 61.9 63.1	2.54 2.53 2.73
Crushed stone (produced in Ako)	G	2.64	0.59	1.53	58.1	6.7

Table 4 Types of Admixtures

Material	Symbol	Composition
Antiwashout admixture	USCA	Water soluble cellulose ether (product of company S)
Superplasticizer	S.P.	High-condensation triazine compound (product of company P)
AE water reducing agent (standard type)	AE ad	Lignosulfonic acid compound polyole complex (product of company P)
AE adjusting agent		Alkyl aryl sulfonate (product of company P)

3. EFFECT OF BINDERS AND ADMIXTURES ON THE BASIC PROPERTIES OF ANTIWASHOUT UNDERWATER CONCRETE

3.1 Effect of Blending Proportion and Characteristics of the Binders

(1) Details of examination

Generally, cement characteristics have a great effect on concrete properties. The antiwashout underwater concrete in this study, with the aim of low-exothermicity and high-flowability, has granulated blast-furnace slag and fly ash added in quantity to reduce exothermicity. In fresh concrete, and in concrete during the hardening process, the reactions of three kinds of binder are considered to occur in parallel. The blending proportion and characteristics of binders affect the properties of the low-heat cement.

Thus, in experiments 1-(1) and 1-(2), the properties of the fresh concrete and the hardened concrete were examined for different blending proportions of the three components and material characteristics.

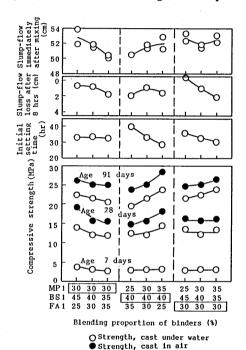
In experiment 1-(1), MP1, BS1 and FA1 were used as binding materials and the slump-flow immediately after mixing, the slump-flow loss, the initial setting time, and the strength were examined by changing MP, BS and FA in 5% increments or decrements. The proportion MP:BS:FA = 30:40:30 was used as the basis.

In experiment 1-(2), the effect of blending proportion of MP1, BS2 and FA1 as the basis was examined. Then the effect of material characteristics on concrete properties was also examined by changing the Blaine fineness of BS2

between $3200 \text{ cm}^2/\text{g}$ and $4100 \text{ cm}^2/\text{g}$, and replacing MP1 with MP2. In this experiment, the adiabatic temperature rise was measured in addition to the characteristics of the fresh concrete and its strength.

(2) Effect of blending proportion of binders

- a) Flowability: Figures 1 and 2 show the results of experiments 1-(1) and 1-(2), respectively. The following trends can be seen in the results of all these experiments:
 - The slump-flow immediately after mixing was greater with less FA.
 - 2) The initial setting time depends on the quantity of MP.



Age 91 days

| Compared to the content of the conte

Fig. 1 Effect of blending proportion of binders on concrete properties (Experiment 1-(1): Fineness of BS2 3800 cm²/g)

Fig. 2 Effect of blending proportion of binders on concrete properties (Experiment 1-(2): Fineness of BS2 3500 cm²/g)

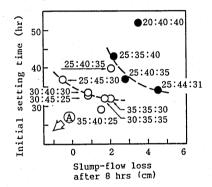
The effect of blending proportion on slump-flow loss differs depending on the kind of granulated blast-furnace slag used. In the case of experiment 1-(1), where the fly ash content was 35%, the slump-flow loss was greater than in cases where the fly ash content was 25% and 30%. In contrast, in experiment 1-(2), where the MP content was 25%, no tendency for slump-flow loss to increase was noticed, even though the fly ash content was increased to 40%. When the MP content was 20% and FA content 40%, the setting time tended to be delayed significantly and the slump-flow loss was greater. We conclude that slump-flow loss is also dependent upon MP content.

To evaluate the effect of blending proportion of binders on the flowability, Fig. 3 shows the relationship between initial setting time and slump-flow loss. By experience, it is considered that the longer the initial setting time the smaller the slump-flow loss. To meet the requirements set out in this study, it

was considered that concrete with little slump-flow loss after mixing (arrow A) would offer better flowability if the initial setting time was the same. The relative positions of the curves allow the flowability to be judged good or bad. For example, when experiment 1-(1) and experiment 1-(2) are compared, the binders in 1-(1), which gives a curve with smaller slump-loss loss for the same initial setting time, would be considered to offer better flowability.

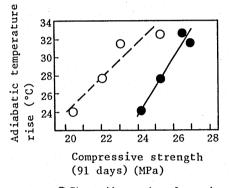
b. Strength: On the basis of measurements at age 91 days, it can be said that the greater the quantity of MP and/or the smaller the quantity of FA, the higher the strength. However, since the growth of strength with age differs depending upon the blending proportion of binders, these characteristics would vary according to how the designed age is decided.

c. Temperature: The adiabatic temperature rise examined in the range of experiment 1-(2) correlates with the strength at age 91 days and in cases with the same kind of binder material there was an approximately linear relationship with the compressive strength, as shown in Fig. 4.



- Experiment 1-Q (Fineness of BS1 3800 cm²/g)
- ①; MP1:BS1:FA1 (Fineness of BS2 ②; MP1:BS2:FA1 3500 cm²/g)

Fig. 3 Relationship between slump-flow loss and initial setting time



- O Strength, cast under water Strength, cast in air
- Fig. 4 Relationship between adiabatic temperature rise and compressive strength (Experiment 1-(2): MP1:BS2:FA1, fineness of BS2 3500 cm²/g)

(3) Effect of fineness of granulated blast-furnace slag and kind of moderate heat portland cement

Figure 5 shows measurements of strength and adiabatic temperature rise when the fineness of the granulated blast-furnace slag was varied. It can be seen from the figure that both the strength and the adiabatic temperature rise were greatly affected by the fineness of BS. Generally, the tendency is that finer BS results in greater strength and exothermicity, while coarser BS leads to less strength and lower exothermicity. In these particular results, the concrete properties underwent a turning point at a fineness of 3500 cm²/g. That is, when finer than 3500 cm²/g, the rise in exothermicity fell while the strength tended to increase abruptly. On the other hand, when coarser than 3500 cm²/g, the tendency for strength to decrease became less significant but exothermicity fell abruptly.

Figure 6 shows the adiabatic temperature rise per unit strength calculated from the change in strength (interpolated using the same curve for MP1 and MP2) and

the change in adiabatic temperature rise with the fineness of the granulated blast-furnace slag, which are shown by broken lines in Fig. 5. When the fineness of BS was about 3400-3500 cm²/g, the adiabatic temperature rise per unit strength was a maximum. Thus, to control heat generation while retaining strength, the fineness of blast-furnace slag can be adjusted in both directions --- either finer or coarser.

Two kinds of portland cement were used in this series of experiments. MP1 and MP2. Although there was no difference in the strength of concrete made using MP1 and MP2, the adiabatic temperature rise of concrete using MPl was smaller than from that using MP2, as shown in Fig. 5. Referring to the characteristics of the materials shown in Table 2, while the mortar strength is about the same in both cases, MP1 has a smaller heat of hydration by 20 J/g for 7-day-old and 9 J/g for 28-day-old mortar and the C2S content is 8% less. It can be inferred that these properties of the portland cements affect the heat generation characteristics of threecomponent cements.

Figure 7 shows the effect of the fineness of granulated blast-furnace slag on the properties of fresh concrete. Although in the range of 2BS fineness between 3200 and 4100 cm²/g a change in fineness has a little effect on slump-flow, the coarser the BS the less the slump-flow loss and the more initial setting was delayed.

3.1 Effect of Admixtures

(1) Details of examination

The authors reported in a previous study[1] that if the amount of AE water reducing agent was changed, the setting characteristics of the antiwashout underwater concrete varied considerably. Experiment (2-(1) was therefore designed to examine the effect of the amount of super-

plasticizer and AE water reducing agent used on the characteristics of slump-flow retention and initial setting time. Further, in experiment 2-(2), the temperature dependency of the slump-flow retention characteristics and initial setting time was investigated.

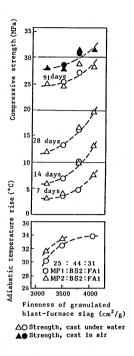
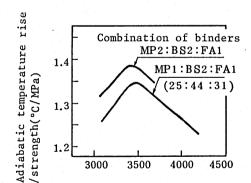


Fig. 5 Effect of fineness of granulated blast-furnace slag and kind of moderate heat portland cement on strength and adiabatic temperature rise



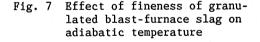
Fineness of granulated blast-furnace slag (cm²/g)

Fig. 6 Effect of finess of granulated blast-furnace slag on strength and adiabatic temperature rise

(2) Effect of amount of admixture

Figure 8 shows the properties of fresh concrete when the content of AE water reducing agent was changed over the range 0-0.4% of the unit binder used, the content of superplasticizer was changed over the range 0-2%. The slump-flow retention increased as the amount of admixture was increased, but the initial setting time was also delayed at the same time. Figure 9 shows that the relationship between slump-flow loss and initial setting time can be described by one curve regardless of the proportion of superplasticizer or AE water Therefore, for low-heat, super-flowable antiwashout reducing agent used. underwater concrete, the required slump-flow retention can be obtained by selecting the appropriate amount of superplasticizer and AE water reducing agent for the mix. However, a substantial improvement in flowability --- that is, improved slump-flow retention while holding the initial setting time constant --- is impossible by adjusting the admixture. This requires an improvement in the binder characteristics or the blending proportion, both factors determining the flowability.

flow 55 50 Immediately Slump after mixing After 8 hrs Slump-flow loss after 8 hrs (cm) 60 Slump-flow loss 50 Initial setting time 3000 3500 4000 Fineness of granulated blast-furnace slag (cm²/g)



(MP2:BS2:FA1=25:44:31)

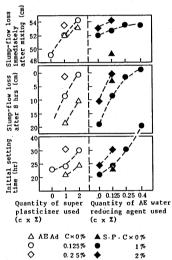
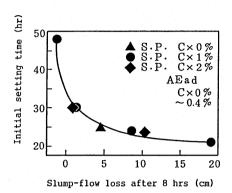
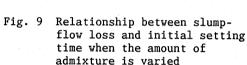


Fig. 8 Effect of amount of admixture used on the properties of fresh concrete

(3) Temperature dependence

Figure 10 shows the properties of the fresh concrete when the mixing and curing temperatures of the concrete were varied between 10°C and 30°C. At higher temperatures, the slump-flow immediately after mixing is larger though the slump-flow loss tends to be greater as setting progresses. When the concrete temperature is low, the slump-flow immediately after mixing is smaller and the initial setting time is delayed.





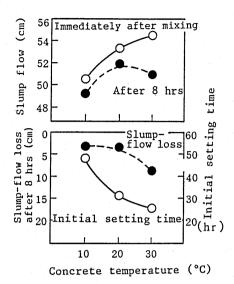


Fig. 10 Effect of concrete temperature on the properties of fresh concrete

4. ADSORPTION OF ANTIWASHOUT ADMIXTURE IN ANTIWASHOUT UNDERWATER CONCRETE AND THE EFFECT OF ADSORPTION ON CONCRETE PROPERTIES

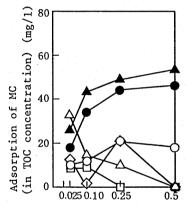
4.1 The Adsorption Phenomenon

The authors confirmed in a previous report[6] that the setting time of antiwashout underwater concrete based on a three-component cement varies according to the kind of binder and fine aggregate used and that the adsorption of antiwashout admixture (MC) by portland cement had an effect on the delay in setting time. In this phenomenon, the amount of MC absorbed by the granulated blast-furnace slag, fly ash, or fine aggregate affects the adsorption of MC by the cement. This in turn alters the reaction of cement in the initial period of hydration, thereby affecting the initial setting time. Different brands of fly ash and kinds of fine aggregate have a particularly great effect on the setting time although these particles should be relatively inactive during the initial stage of hydration.

In the previous report, the concentration of MC solution used in measuring the rate of MC adsorption was 0.025%. Although antiwashout underwater concrete generally contains 2-3 kg/m³ of MC, it is difficult to know the concentration of MC when it takes part in adsorption. Also, since the adsorption phenomenon is related to the concentration of adsorption material, in this study the change in amount of adsorption of material by varying the concentration of MC solution was measured. Although 1.0%-1.1% of MC to the amount of water per 1 m³ of concrete is used in antiwashout underwater concrete, not all the MC added is necessarily dissolved in the water. In the case where MC acts on the bulk of concrete other than coarse aggregate, assuming coarse aggregate quantity is $_3$ 1000 kg/m², specific gravity 2.65, air volume 4% and MC quantity 2.3 kg/m, the weight concentration per mortar volume of MC becomes 0.4%(=2.3/[960-(1000/2.65)]).

Figure 11 shows the amount of MC adsorption by cement and fine aggregate when the concentration of MC solution is varied from 0.025% to 0.5% as measured by the total organic carbon content (TOC concentration). For both cement and fine aggregate the adsorption amount is approximately constant for MC solutions higher than 0.25%. On the other hand Fig. 12 shows the results of examining two kinds of fly ash (A and B) and two kinds of granulated blast-furnace slag (a and b) for which distinctive behavior was obtained in the previous report. Results indicate that the adsorption of MC by cement in coexistence with fly ash is approximately constant for MC solutions higher than 0.25%, as with cement alone. While the difference between fly ash A (with which adsorption of MC by cement increased) and fly ash B (with which adsorption of MC by cement decreased) is distinctive, the amount of MC adsorption by cement when blast-furnace slag is present tended to increase abruptly as the concentration of MC solution rises. This phenomenon is common to both granulated blast-furnace slags a and b. In the domain where the concentration of MC solution exceeds 0.25%, when granulated blast-furnace slag is present, a far greater amount is adsorbed by cement than when there is no blast-furnace slag.

Although the mechanism by which the characteristics of granulated blast-furnace slag such as these affect the antiwashout underwater concrete has not yet been examined, it was confirmed that when the concentration of the MC solution is high, the delay in setting can be explained in terms of adsorption of MC by cement alone or in coexistence with fly ash and fine aggregate.

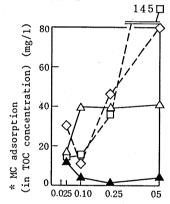


Concentration of MC solution (%)

- Adsorption by simple cement
- Adsorption by fine aggregate
 Adsorption by simple admixtures

$$\triangle$$
 FA-A \diamondsuit BS-a \blacktriangle FA-B \square BS-b

Fig. 11 Relationship between amount of MC adsorption by mateterials and concentration of MC solution



- * Amount of MC selectively adsorpted. Concentration of MC solution (%) by cement in the coexistence of cement and admixture
 - △ Cement + FA-A
 - ▲ Cement + FA-B
 - ♦ Cement + BS-a
 - □ Cement + BS-b

Fig. 12 Relationship between amount of MC adsorption by cement and concentration of MC solution

4.2 Effect of Adsorption of Antiwashout Admixture by Fine Aggregate on Concrete Properties

(1) Details of examination

Previous examinations[6] by the authors demonstrated that the setting time varied according to the granular characteristics of the fine aggregate and the mineral composition of the granular content. The effect of the adsorptive clay was especially large.

It is well known that the particle size of some aggregate varies depending upon the location where the sea sand was obtained, so in experiment 4-(2) the effect of fine aggregate particle size on the properties of antiwashout underwater concrete was examined. Also, since a phenomenon has been observed in which the antiwashout admixture adheres to the surface of most fine aggregate, forming a lump during dry mixing, the effect of such surface moisture on the concrete properties was examined in experiment 4-(1) prior to undertaking experiment 4-(2).

(2) Effect of fine aggregate with surface moisture

In experiment 4-(1), the antiwashout underwater concrete was mixed in the conventional way, that is, batched water and agents were added after dry mixing the binder, aggregate, and antiwashout admixture.

In mixing trials during tests, the fine aggregate is usually in a saturated surface-dry condition and materials are added en masse. When adding the antiwashout admixture before dry mixing two methods are involved.

- 1) Throw in antiwashout admixture over the fine aggregate
- 2) Premix antiwashout admixture into the binders

The method used depends on the testing organization. In general (concrete mixing plant) the antiwashout admixture is thrown in from above the fine aggregate bin after weighing, and is dry mixed together with the fine aggregate to disperse it. The surface moisture of fine aggregate is normally 4-8%. In our experiments, four cases were examined (premix antiwashout admixture into fine aggregate or into binders) x (fine aggregate with dry surface or with moist surface). Two types of mixers were used, a pan-type forced mixer and a horizontal dual-axis forced mixer, and the characteristics of the results were confirmed.

Figure 13 shows the test results. Similar results were obtained for both types of mixers. That is, when the antiwashout admixture was premixed into the fine aggregate and there is surface moisture present, the following trends were recognized:

- 1) The scatter in slump-flow immediately after mixing increases.
- 2) Slump-flow loss after 8 hours increases.
- Initial setting occurs earlier.

In contrast, when the antiwashout admixture is premixed into the binders, trends are the following even if the fine aggregate contains surface moisture:

- 1) There is no change in slump-flow loss.
- The initial setting time is unchanged or somewhat delayed.

Therefore, if fine aggregate with surface moisture is to be used, ideally it should be premixed into the binders to give better slump-flow values.

(3) Effect of fine aggregate particle size

Four grades of fine aggregate from the same location with different particle sizes plus two grades of fine aggregate that were sieved to less than 0.15 mm

fineness were used. The range of FM was 2.40-2.75. The surface moisture was adjusted to within the range 5-6% and the mixing method used was to add the antiwashout admixture by throwing it over the fine aggregate, dry mix them together with the binder and coarse aggregate, and finally pour in the batched water.

Figure 14 shows the test results. It was seen that the greater the granulated content in the fine aggregate the larger the slump-flow loss. Although granulated content was defined as silt smaller than 0.074 mm and fine particles smaller than 0.15 mm in this case, slump-flow loss and granulated content showed good correlation. This led us to consider that a standard sieve test could be applied to control the particle size of the fine aggregate. With regard to the slump-flow immediately after mixing and the setting time, no significant variation was recognized within this range of particle size.

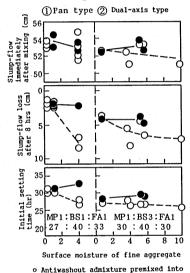
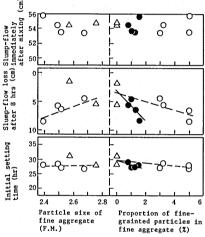


Fig. 13 Effect of surface moisture and method of adding antiwashout admixture on the properties of fresh concrete

fine aggregate
Antiwashout admixture premixed into



- Proportion of fine-grained particles below 0.074. mm
- O Proportion of fine-grained particles below
- △ Aggregate removed particles below 0.15 mm from sieve
- Fig. 14 Effect of particle size and amount of fine-grained e aggregate on the properties of fresh concrete

It is considered that slump-flow loss in these experiments can be explained by the adsorption of antiwashout admixture. In other words, the antiwashout admixture that should help retain slump-flow by adsorption by the cement is actually adsorbed on the surface of the fine aggregate, making it ineffective.

The initial setting time did tend to be shorter (changing it by about 3 hours in these experiments) as the proportion of fine-grained aggregate increased, but the effect of this fine-grained aggregate appears to have had a more remarkable effect on the slump-flow loss.

5. EFFECT OF MIXING METHOD ON ANTIWASHOUT UNDERWATER CONCRETE

(1) Details of examination

Determining at which stage of the concrete production process the adsorption of antiwashout admixture occurs within the binder-water-fine aggregate system is difficult because the antiwashout admixture cannot be observed once mixed.

However, when the antiwashout admixture is dry-mixed into the fine aggregate, the presence or otherwise of surface moisture governs the flowability, while the effects of surface moisture can be disregarded if the antiwashout admixture is premixed into binders. This implies that adsorption begins as soon as dry mixing starts. In actual construction work, the binder, fine aggregate with surface moisture, and the coarse aggregate are dry mixed, meaning that loss of flowability will tend to occur. Also dry mixing increases the overall mixing time. In an attempt to solve the problems of dry mixing, mixing methods were examined. In order to secure concrete flowability and to reduce the dry mixing time, the antiwashout admixture was thoroughly dispersed in the binder before mixing.

In experiment 5-(1), the method of adding the antiwashout admixture, whether there is time for dry mixing or not, and mixing time were tested and the effect of these on properties of the concrete was examined.

In experiments 5-(2) and 5-(3), comparisons were made on the properties of concrete when the standard mixing method (throw in antiwashout admixture over the fine aggregate and dry mix) and the premixing method (premix antiwashout admixture into the binders and mix without dry mixing) and the following methods were executed.

- 1) First mix the mortar and then add coarse aggregate.
- Add water in two batches, one at the time of mortar mixing and the other when coarse aggregate is added.

In experiment 5-(4), the effect of dividing the mixing water on the properties of the mortar was examined.

Figure 15 shows the method of mixing implemented. In experiments 5-(1) and 5-(4), the surface moisture in all fine aggregates was adjusted to 5%. When premixing the antiwashout admixture into the binders, the method adopted was to put the entire batch quantity of the three kinds of binder and the antiwashout admixture into a vinyl bag and thoroughly mix them. Also, in experiments 5-(2) and 5-(3) an omni-mixer was used to stir the mixture for 30 seconds.

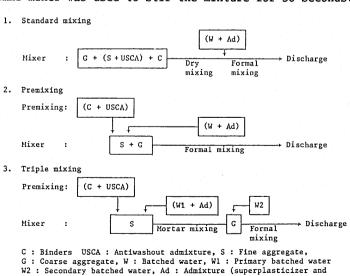
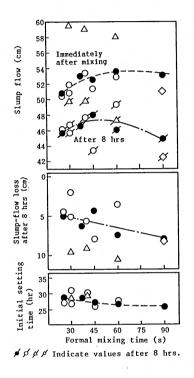


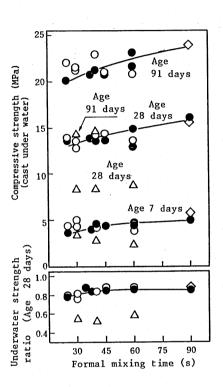
Fig. 15 Mixing method for antiwashout underwater concrete

AE water reducing agent)

(2) Properties of antiwashout underwater concrete when the antiwashout admixture is premixed

Figures 16 and 17 show the results of experiment 5-(1). Four methods of adding the antiwashout admixture was used, (premix antiwashout admixture into aggregate or binders) x (dry mix or without dry mixing); and the mixing time (called formal mixing time throughout) after adding the batched water was varied from 25 seconds to 90 seconds.





- Dry mixing 15 s, premix antiwashout admixture into binder o Dry mixing 0 s, premix antiwashout admixture into binder
- Δ Dry mixing 0 s, premix antiwashout admixture into fine aggregate
 ⋄ Dry mixing 15 s, premix antiwashout admixture into fine aggregate

Fig. 16 Effect of mixing time and method of adding antiwashout admixture on properties of fresh concrete

Fig. 17 Effect of mixing time and method of adding antiwashout admixture on concrete strength

When the antiwashout admixture was premixed into the binders and dry mixed, a certain relationship was noted between the formal mixing time and concrete properties.

As the formal mixing time increased,

- 1) slump-flow loss immediately after mixing increased,
- 2) slump-flow loss after 8 hours increased,
- 3) setting time accelerated, and
- 4) the strength improved.

However, these properties tend to converge to a limiting value as the formal mixing time increases further, and the results of mixing for 60 seconds and 90 seconds are almost equal.

A longer formal mixing time means greater strength, which is favorable from the viewpoint of hardened concrete properties. However, the slump-flow loss of the fresh concrete is more severe. The setting time tends to be earlier, although the change is small.

A comparison of the mixing methods yields the following results over the range of formal mixing time between 25 seconds and 60 seconds:

- 1) When the antiwashout admixture is premixed into the fine aggregate, separation of the mortar and aggregate occurs unless dry mixing is carried out. In other words, slump-flow immediately after mixing is greater. This is thought to be due to the fact that, as the antiwashout admixture does not disperse uniformly into the concrete, the required increase in viscosity does not happen. In this case, as the antiwashout admixture does not operate effectively, the slump-flow loss is also greater and the strength of concrete cast under water is reduced. No improvement was seen even when the mixing time was extended.
- When the antiwashout admixture is premixed into the binders and then thrown in, no segregation of materials occurs even though there is no dry mixing, and the properties of fresh concrete and strength are about the same as in the case when the materials were dry mixed. However, some scatter between batches were noted.

As before, by premixing the antiwashout admixture into the binders it is possible to produce a concrete about equal to that yielded with dry mixing, but without having to actually dry mix. However, since some scatter was observed, it will be necessary to determine the extent of scatter.

(3) New mixing method for antiwashout underwater concrete

The main characteristic required of low-heat, super-flowable antiwashout underwater concrete is good flowability, so it is necessary to stabilize quality while maintaining flowability. Experiment 5-(2) was to examine a mixing method that meets these requirements.

As a result of exhaustive examinations, concrete with excellent flowability was obtained using a dual-axis forced mixer and the following mixing method:

- 1) Premix antiwashout admixture into binders.
- Add a part of the batched water to binder and fine aggregate, mix in mortar to form the appropriate viscosity.
- Add coarse aggregate along with the remaining water to complete mixing.

This mixing method uses three stages of mixing to produce concrete, so it is named the "Triple Mixing Method." The reason for premixing the antiwashout admixture into the binders in 1) is to thoroughly disperse the antiwashout admixture into the binders, thereby saving dry mixing time. 2) is aimed at dispersing the antiwashout admixture in the binder-fine aggregate-water system.

Generally, when a standard concrete mixer is used to mix antiwashout underwater mortar at the same speed as in the case of ordinary concrete, it is necessary to extend the mixing time to obtain mortar of the required quality. This is

because the mortar is extremely soft mixing, so the frictional shear force exerted on it by the blades of the mixer, and the frictional shear force within the fine aggregate itself, is small. Adding the water in two batches, as here, is thought to strengthen mixing by making the mortar harder during the initial stage of mixing and to enhance dispersion upon contact between antiwashout admixture-binder-fine aggregate and water.

Figure 18 shows the results of experiment 5-(4). The experiment measured the effects of the water division ratio on mortar characteristics using a planet-

movement 10-liter mortar mixer. Although a direct evaluation of mixing is not possible as this is not a concrete mixer, any trend which points to an optimum division in terms of resultant slump characteristics can be seen. Within the range of this experiment, strength tended to increase as less water was added in the primary batch.

(4) Effectiveness of the triple mixing method

Figures 19 and 20 show the results This is a of experiment 5-(2). comparison of the standard mixing method (antiwashout admixture and fine aggregate are thrown into the mixer, and dry mixed with binder and coarse aggregate), the premix mixing method (antiwashout admixture premixed into binders and without dry mixing) and the triple mixing method, mixing for an equal time after contact between the binders and batched water. At the same time, the results of changing the ratio of the primary batch of water between 0.8 and 1.0 for the triple mixing method are shown.

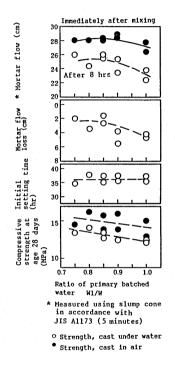


Fig. 18 Effect of 2-step addition of water on the properties of mortar

In the case of the standard mixing method, the slump-flow loss 8 hours after mixing was about 10 cm, while the loss was smaller with the premix method and the triple mixing method. When all the water was added at one time in the triple mixing method, the tendency was far greater slump-flow loss as compared with the case where the proportion was 0.8W and 0.9W.

With regard to strength, the tendency was for this to be somewhat lower in the premixing method and the triple mixing method when the primary batched of water was 1.0W.

Figures 21 and 22 show the properties of fresh concrete and strength in the case where the formal mixing time was changed for each mixing method.

In the case of standard mixing, the longer the formal mixing time the greater the slump-flow loss, while in other two cases no such tendency was noted within the range of mixing times tested.

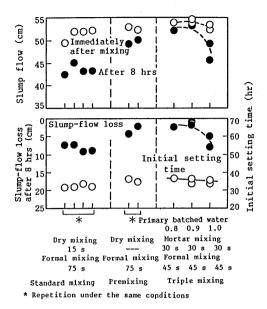


Fig. 19 Effect of method of mixing on the properties of fresh concrete (with same formal mixing time)

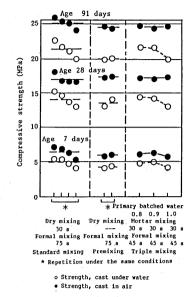


Fig. 20 Effect of method of mixing on concrete strength (with same formal mixing time)

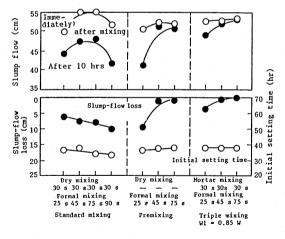


Fig. 21 Effect of mixing method on the properties of fresh concrete (with varied mixing time)

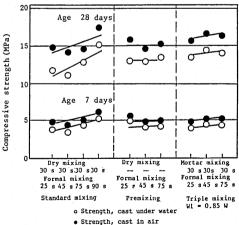


Fig. 22 Effect of mixing time on concrete strength (with varied mixing time)

In the premixing method a formal mixing time of 25 seconds was insufficient and slump-flow loss was considered to have occurred. In the standard method, formal mixing times of 45 and 75 seconds tended to yield a large slump-flow immediately after mixing. Since the measured value of strength of the concrete cast under water at that time was small, it may be that the antiwashout admixture had not dispersed thoroughly into the concrete because the mixing time was too short.

Generally speaking, it was confirmed that, while with standard mixing and premixing method the properties of fresh concrete and strength were greatly affected by the mixing time, concrete of stable quality could be obtained using the triple mixing method.

6. ACTION OF ANTIWASHOUT ADMIXTURE IN HARDENED CONCRETE

(1) Details of examination

The low-heat properties of antiwashout underwater concrete with high slag content cement have been reported[8],[9] in addition to the three-component cement used in this study. Investigations of strength and adiabatic temperature rise in concrete using high slag content cement and examinations of the optimum blending proportion of granulated blast-furnace slag[7] show that for ordinary concrete without antiwashout admixture, the compressive strength suddenly drops when the slag blending proportion exceeds 80%. For antiwashout underwater concrete, 90% slag content yielded about the same strength as 91-days concrete with 0% blending proportion. This mechanism can be attributed to the fact that addition of antiwashout admixture improves water retainability, restricting bleeding, and therefore limiting the loss of alkali content from the concrete and uniformly distributing alkali to accelerate slag reaction. However, the authors consider that the long-term effects of granulated blast-furnace slag are a result of Ca(OH)₂ generated by the reactions of portland cement and not the initial alkali content, which could be governed by bleeding.

Therefore, in high slag content cement, we consider that some sort of peculiar chemical reaction must occur in the portland cement-granulated blast-furnace slag-antiwashout admixture system. Consequently, in this chapter, the effect of adding antiwashout admixture, or otherwise, on the strength and heat generation is investigated for various cements, including high slag content cement. The action of antiwashout admixture on the hardened concrete is considered from various angles, including chemical methods.

In experiment 6-(1), ordinary portland cement, blast-furnace cement of blending proportion 50-90%, fly ash cement, and three-component cement are studied for the effects of the presence of antiwashout admixture on the strength.

The experiment simply aimed to investigate the effects of the presence of antiwashout admixture, so the mix proportion of all other materials was the same. However, because with ordinary concrete air entrainment becomes difficult with granulated blast-furnace slag and fly ash, the amount of air entraining agent was adjusted for each mix proportion to keep the air volume uniform. Approximate test conditions and results were the following: unit cement quantity 400 kg/m^3 , unit water quantity 180 kg/m^3 , slump immediately after mixing, depending on the type of cement used, was in the range 15.1-23.5 cm in the case of ordinary concrete, and 10.1-24.1 cm where antiwashout admixture was used. Air volume was in the range 3.5-4.6%.

In experiment 6-(2), using mortar without coarse aggregate from the mixes of 6-(1), the characteristics of temperature rise were examined using a simple heat measuring instrument (Fig. 24). The instrument was not completely thermally

insulated, so the radiation characteristics of the device itself were measured, and by adding the accumulated heat radiation to the measured value, the adiabatic temperature rise was estimated. The ambient temperature at the time of the measurements was 20°C. In estimating temperature rise, thermal conductivity in the heat-generating body and the insulation material was disregarded and the temperature rise was evaluated in terms of the maximum interior temperature and surface heat radiation only. Therefore, since differences in the thermal properties of different mortars have not been taken into consideration, there may be some errors in the comparison by kind of binder. However, since the mix proportion and materials other than the binder are the same, there should be no problems in making comparisons with or without antiwashout admixture. On some binders, the heat of hydration was measured by means of the heat of dissolution method.

(2) Effect of antiwashout admixture on strength

Figure 23 shows the measurements of strength for both mixes with and without antiwashout admixture for various binders.

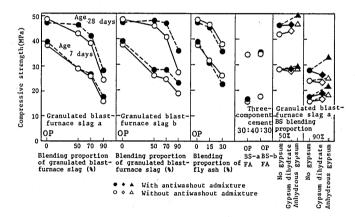


Fig. 23 Effect of antiwashout admixture on concrete strength

Practically no difference was seen with and without antiwashout admixture for ordinary portland cement. On the other hand, where granulated blast-furnace slag was added, the addition of antiwashout admixture increases the strength, the extent of the change depending upon the brand and blending proportion of the slag. In the case of BS-a, the increase in strength was 3-4 MPa at age 28 days in the blending proportion 50-90%. On the other hand, when BS-b was substituted, the greater the blending proportion, the more the strength improved and when the proportion reached 90% the increase in strength was 9 MPa over that for the mix without antiwashout admixture.

The biggest difference between BS-a and BS-b from the viewpoint of material characteristics lies in the fact that BS-b contains gypsum (Table 2), so the strength was also measured in the case where gypsum was added to BS-a. The amount of gypsum added was about the same as the quantity in BS-b (2% by SO_3).

When gypsum dihydrate was added, the strength was no different from when no gypsum was added, and no change was seen whether antiwashout admixture was added or not, while, on the other hand, when anhydrous gypsum was added, there was a tendency for strength to improve if antiwashout admixture was included. Therefore, it is assumed that some action of the anhydrous gypsum (in the

granulated blast-furnace slag) on the antiwashout admixture leads to the increase in strength. On the other hand, a qualitative analysis of granulated blast-furnace slag (BS-b) by using X-ray diffraction indicated gypsum dihydrate. Despite the various studies[9] that have been carried out on the action of gypsum in blast-furnace slag cement, the effects of different types and quantities on the strength has not yet been clarified. The action of gypsum on antiwashout admixture, as described, appears to differ depending on the type of granulated blast-furnace slag or gypsum. It is also possible that the characteristics change according to the fineness. Therefore, great care must be exercised when the aim is low heat generation through adding granulated blast-furnace slag to antiwashout underwater concrete. In the case of fly ash cement, strength is reduced somewhat when antiwashout admixture is added. Although in a three-component cement, it is recognized that strength tends to increase when antiwashout admixture is added, the extent of this change is not so great as the case of blast-furnace slag cement. This may be because tendency of granulated blast-furnace slag to increase strength is offset by strength-reducing effects of fly ash.

(3) Effect of antiwashout admixture on heat generation

Figure 24 shows the estimated values of adiabatic temperature rise for various binders and measured values of heat of hydration using the heat of dissolution method.

When antiwashout admixture is added, the heat generated increased for all binders examined here. Where the blending proportion of granulated blast-furnace slag was 50%, the increase was large, with a rise of 12°C for BS-a and for a 90% proportion of BS and in the case of the three-component cement a rise of $4\text{-}6^{\circ}\text{C}$ was seen. In ordinary portland cement, which showed no change in strength by the addition of antiwashout admixture when mixed as concrete, and in fly ash cement, which decreased in strength, a rise in temperature of about 2°C was seen. Measurements of heat of hydration confirmed that the heat of hydration increases when antiwashout admixture is added to all 4 kinds of binder.

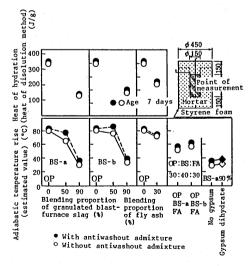


Fig. 24 Effect of antiwashout admixture on heat generation of concrete

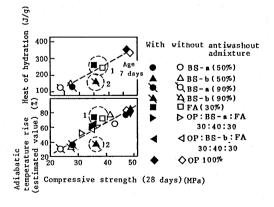


Fig. 25 Effect of antiwashout admixture on the relationship between strength and heat generation

Figure 25 shows the relationship between measured values of strength, adiabatic temperature rise and heat of hydration. Other than in the cases of fly ash cement and high slag content cement (shown in the figure with 1 and 2) both heat generation and strength increased when antiwashout admixture was added. In other words, it can be concluded that the addition of antiwashout admixture accelerates the cement reaction. However in the case of fly ash cement, when antiwashout admixture was added, the heat generation increased and strength decreased, while in the case of high slag content cement, for a given heat generation, the strength was greater. Therefore although heat generation increases with the addition of antiwashout admixture, the relationship of this increase to the strength differs according to the kind of binder, and our conclusion is that the relationship GRANULATED BLAST-FURNACE SLAG > PORTLAND CEMENT (no change upon addition of antiwashout admixture) > FLY ASH clearly exists within the range of these experiments.

(4) Effect of antiwashout admixture on hydration reaction

To clarify the cause of the increased heat generation when antiwashout admixture is added, and the increase in strength when granulated blast-furnace slag is included, the concentration of various ions in the pore solution of hardened concrete was measured. Also the hydration ratio was calculated by measuring the ignition loss from hardened concrete. Figure 26 shows the results.

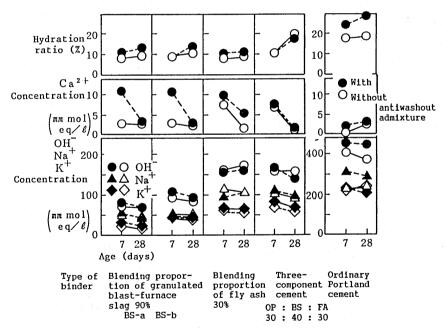


Fig. 26 Effect of antiwashout admixture on hydration ratio and ion concentration in pore solution

In high slag content cement, the behavior of calcium ions (${\rm Ca}^{2+}$) in the pore solution was peculiar. When antiwashout admixture was added, the ${\rm Ca}^{2+}$ concentration at age 7 days was about 4 times higher than with no admixture. However, this excess of ${\rm Ca}^{2+}$ disappeared by 28 days, when the difference between the two samples became practically none. Therefore, it can be implied that in high slag content cement with antiwashout admixture, a phenomenon occurred which means the solubility of ${\rm Ca}^{2+}$ early on is very high due to some action of the

antiwashout admixture and that a reaction occurs which absorbs this ${\rm Ca}^{2+}$ by the age of 28 days. How behavior such as this affects the strength and heat characteristics of the concrete and why the solubility of ${\rm Ca}^{2+}$ increases, remains to be solved in future investigations.

The hydration ratio of concrete with antiwashout admixture tends to be larger than that without it. Taking this into consideration when analyzing the increase in heat of hydration as confirmed in the previous section, it can be said that the addition of antiwashout admixture accelerates the hydration of the binder itself. On the other hand, with fly ash cement and ordinary portland cement, there is a possibility that some phenomena take place which prevent an increase in strength, since no increase in strength was seen even though antiwashout admixture was added.

7. CONCLUSIONS

The results of the studies may be summarized as follows:

- The basic properties of antiwashout underwater concrete (flowability, setting time, strength, and adiabatic temperature rise) are greatly affected by the properties of the cement, granulated blast-furnace slag, fly ash, and the blending proportion of these. To obtain an antiwashout underwater concrete that satisfies the basic requirements in accordance with established conditions, it is necessary to select appropriate kinds of binder and determine the blending proportion through trial mixing.
- 2) By increasing or decreasing the amount of superplasticizer and air-entraining water-reducing agent it is possible to adjust the changes of setting time and slump-flow retention time.
- 3) The amount of fine grained material in the fine aggregate greatly affects the changes of slump-flow. It is necessary to manage the particle size distribution of the fine aggregate and to pay attention to the mixing in of adsorptive clay.
- 4) When surface moisture exists on the fine aggregate, and when it comes into contact with the antiwashout admixture, the admixture forms a lump on the surface. The effect of the admixture, which should primarily act on the binder, was impaired and flowability became lower. To prevent this from occurring, it is best to produce a concrete without dry mixing. By premixing the admixture into the binders and adding this mixture to the mixer, a similar dispersion of admixture is obtained as by dry mixing.
- 5) A mixing method which further stabilizes concrete properties and improves flowability is the triple mixing method. (1) premix the binders and the antiwashout admixture, (2) disperse antiwashout admixture using a mortar mixing for binders antiwashout admixture fine aggregate system, and (3) a concrete mixing for mortar coarse aggregate system.
- 6) In fresh concrete, the adsorption of antiwashout admixture by the component materials affects the flowability and setting characteristics, and the changes in concrete properties with different mixing methods can be explained in terms of the adsorption phenomenon.
- 7) In some cases, the antiwashout admixture accelerates the hardening reaction, depending on the kind of admixture used, and its interaction with granulated blast-furnace slag is particularly remarkable. However, care must be exercised as this effect differs according to the kind of

granulated blast-furnace slag and gypsum. It may be that the behavior of calcium ions in early age concrete plays some role in the phenomenon.

ACKNOWLEDGEMENTS

In the implementation of these studies, Professor Hajime Okamura, Engineering Department of Tokyo University has given us instructive suggestions. And in obtaining materials and carrying out experiments, valuable assistance was given by Nihon Cement Co., Ltd., Dailchi Cement Co., Ltd., Shin-estsu Chemical Co., Ltd. Pozzolis Bussan Co., Ltd., and Kitagawa Iron Works, Ltd. We wish to take this opportunity to express our thanks to these people and organizations.

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